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INORGANIC CHEMISTRY

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FOURTH EDITION—REVISED

PREFACE TO THE
FOURTH ENGLISH EDITION

In this edition the general scheme, which proved such an attractive feature of earlier editions, has been maintained. It may perhaps be pointed out to the new reader that this work is designed to include a great deal of information as concisely as possible and yet to present it in a palatable form. The materials of inorganic chemistry are dealt with collectively rather than individually, with a consequent saving of space and of fatigue to the reader.

The whole of the text has been thoroughly revised for this edition and the improvements are more extensive than the increase in size of a dozen pages might suggest. Substitution rather than addition has been the rule, and further use has been made throughout of modern concepts and notation of valency. Recent work on radioactivity and isotopes has been included, as have also descriptions of new compounds and reactions published since the last edition.
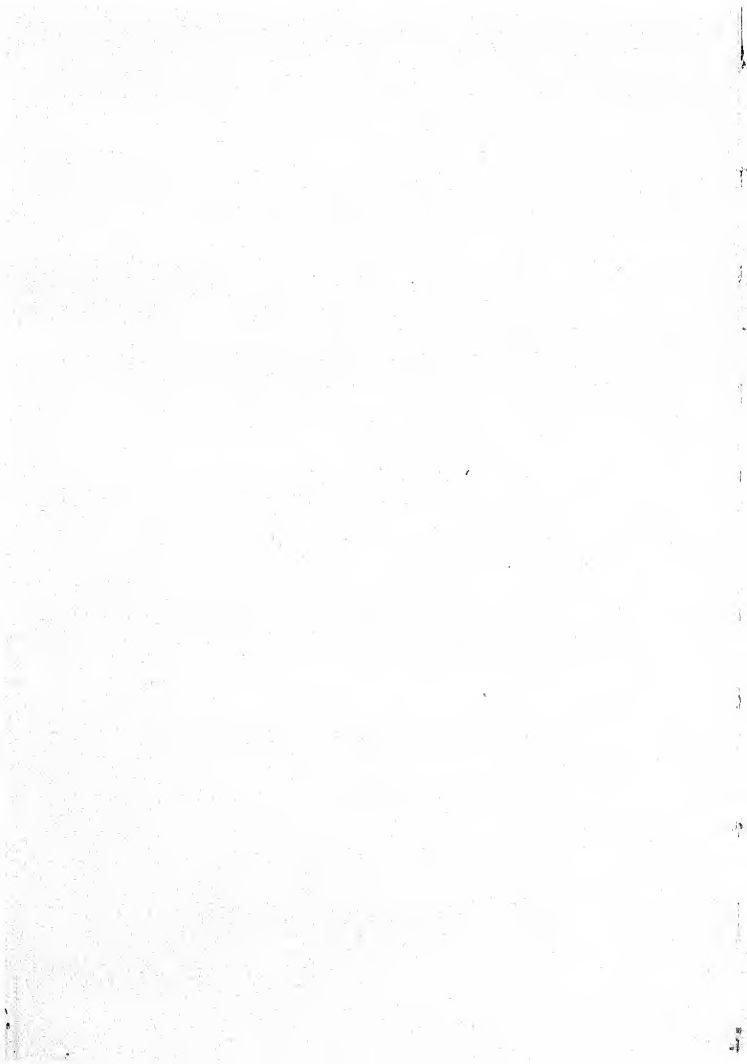
The figures on pp. 123, 755, and 842 have been copied from the Annual Reports on the Progress of Chemistry by permission of The Chemical Society and of the authors of the articles; those on p. 305, from *Nature*, by permission of the Editor.

We have to thank Mr A. Hebdon, B.Sc., F.I.C., of the Chemistry Department, Chelsea Polytechnic, for assistance in preparing the new index, reading the proofs and for useful suggestions.

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I. THE ELEMENTS

CHAPTER I

THE STRUCTURE OF MATTER

Structure of atoms—Structure of molecules—Structure of crystals—
Crystal structure of the elements—Electron diffraction

1. The Structure of Atoms

THE name atom (from ἄτομος, indivisible) is no longer appropriate for the chemical units of matter, for although atoms cannot be decomposed by the usual chemical processes, experiments have shown that they are composite structures made up of constituent parts, and that transmutations of atoms can be effected. The detailed structure of atoms will be first considered, as their properties, and hence those of the elements, depend on it. The greater part of the work on atomic structure belongs to the science of physics, and the treatment which follows will be confined to those details which are essential for an understanding of chemical properties. The boundaries of chemistry and physics are becoming, however, increasingly difficult to define.[1]

The conception of the structure of the atom is based on a mass of experimental work by many investigators,[2] particularly that of Lord Rutherford.[3] The results are best exhibited in the Rutherford-Bohr atom model.[4] According to this theory, the atom consists of a nucleus bearing a positive charge of electricity, surrounded by negatively charged electrons. The number of free positive charges on the nucleus (atomic number, p. 8) is equal to the number of the surrounding electrons, so that the atom is externally electrically neutral. Almost the whole of the mass of the atom is concentrated in the nucleus, the mass of an electron being only $\frac{1}{1844}$ of that of a hydrogen atom.

The structure of the atom can be investigated to some extent by bombarding it with particles possessing sufficient energy and of suitably small size. These particles are provided by the radioactive substances

[1] See, for example, H. A. Wilson, *Modern Physics*, London, 1937.
[2] Cf. *The Structure of the Atom*, E. N. da C. Andrade, 3rd ed., London, 1927.
[3] *Phil. Mag.*, 1911, 21, 699 ; 1914, 27, 488.
[4] *Phil. Mag.*, 1913, 26, 1, 476, 857.

A

The same type of expression is used to calculate the series of lines in the spectrum of an element; this was first done for the hydrogen spectrum by Balmer, and then Rydberg pointed out the general application of this constant to all series spectra. The factor $3 \cdot 290 \times 10^{15}$, which is of universal importance, is known as Rydberg's constant (R). The constant is also derived from the quantum theory, and this is almost a proof that the spectral lines are due to energy changes in quanta. The Rutherford-Bohr atom model is thus interlinked with an hypothesis from which observed spectrum lines can be predicted.

The atom may therefore be pictured as a planetary system with the nucleus as the sun and the electrons as planets moving in elliptical orbits. The circle, as the simplest ellipse, is also a possible orbit in the atomic system. The orbit nearest the nucleus is described as the K-level, the next as the L-level, the third as the M-level, and so on. The K series of orbits are one-quantum, the L two-quantum, and so on. The elliptical and circular orbits are shown diagrammatically in Fig. 1. Each of the elliptical orbits has obviously two characteristics—the major and the minor axis, the major axis being of the same length for orbits of the same quantum number, while the minor axes equal the major axes as a maximum in the circular orbits. This is indicated by the notation 4_1, 4_2, 4_3, 4_4, taking the 4-quantum orbits as an example. In the M-quantum level there are m orbits and the m_m orbit is a circle.

The two quantum numbers (n_k, n being the principal quantum number and k the azimuthal quantum number) used by Bohr have proved to be insufficient to account for the complexity of the lines in the hydrogen spectrum, and four quantum numbers[1] have become necessary to explain various phenomena. They are described and represented as follows, and are governed by Pauli's exclusion principle,[2] namely that two electrons cannot exist in a given atom with all four quantum numbers identical :

(1) Principal or total quantum number, represented by n and corresponding to n in Bohr's notation.

(2) Serial quantum number, corresponding with the k term of Bohr, but in this notation represented by l and having the values of $n-1$, $n-2$, etc. . . . o, for a given value of the principal quantum number n. This second quantum number is called the serial number because it is concerned with the spectral series (sharp, principal, diffuse, fundamental).

(3) Magnetic quantum number, m_l. This defines the orbits of the electrons in magnetic fields and has the values l, $l-1$, $l-2$, . . . o, $-(l-1)$, $-l$, i.e. $2l+1$ values, for each value of the serial number.

(4) Spin quantum number, m_s, which defines the direction of the electron spin in a magnetic field ; it has the value $+\frac{1}{2}$ or $-\frac{1}{2}$, there being two directions of rotation with a quantum difference of unity.

These rules can be used to fix the maximum number of electrons which can occupy an n_k sub-group; for example a 3_2 group on Bohr's

[1] Hund, *Zeit. f. Physik.*, 1925, **33**, 345.   [2] *Ibid.*, 1925, **31**, 765.

notation, in Hund's system has $n = 3$; $l = 1$; $m_l = 1, 0, -1$; $m_s = +\frac{1}{2}, -\frac{1}{2}$. There are thus a maximum of 6 electrons in a 3_2 group, with quantum numbers—

$n =$	3	3	3	3	3	3
$l =$	1	1	1	1	1	1
$m_l =$	1	1	0	0	-1	-1
$m_s =$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$

Generally, the maximum number of electrons in an n_k group is $2(2l+1)$ or $2(2k-1)$, the maximum numbers which the sub-groups can contain being:

level n_k	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4
l	0	0	1	0	1	2	0	1	2	3
Maximum number of electrons	2	2	6	2	6	10	2	6	10	14
Total in each principal group .	2	8		18			32			

The table on p. 6 shows the distribution of electrons in the atoms following these rules; Main Smith[1] and Stoner[2] arrived at this distribution prior to Hund's establishing these rules, Main Smith basing his conclusions on chemical evidence and Stoner on spectral and magnetic results. For many purposes, a consideration of only the principal quantum number is necessary.
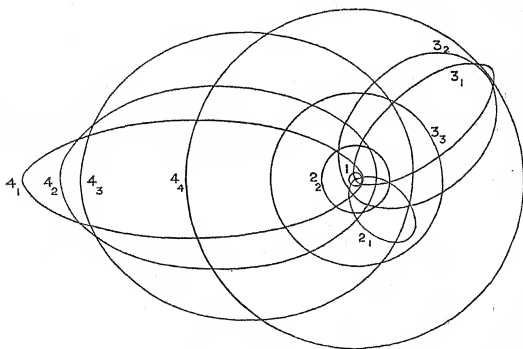
FIG. 1.

The positive charge on the hydrogen nucleus (the proton) is unity. The number of surrounding electrons must also be one, in order that its external neutrality may be preserved. The charge on the nucleus, and consequently the number of electrons in the orbits, increases by unity

[1] *Chemistry and Industry*, 1924, 43, 323.   [2] *Phil. Mag.*, 1924, 48, 719.

The Grouping of the Electrons in the Atoms of the Elements

Level: K | L | M | N | O | P | Q

Element	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	6_1	6_2	6_3	7_1	7_2
1 H	1																		
2 He	2																		
3 Li	2	1																	
4 Be	2	2																	
5 B	2	2	1																
6 C	2	2	2																
7 N	2	2	3																
8 O	2	2	4																
9 F	2	2	5																
10 Ne	2	2	6																
11 Na	2	2	6	1															
12 Mg	2	2	6	2															
13 Al	2	2	6	2	1														
14 Si	2	2	6	2	2														
15 P	2	2	6	2	3														
16 S	2	2	6	2	4														
17 Cl	2	2	6	2	5														
18 A	2	2	6	2	6														
19 K	2	2	6	2	6		1												
20 Ca	2	2	6	2	6		2												
21 Sc	2	2	6	2	6	1	2												
22 Ti	2	2	6	2	6	2	2												
—																			
28 Ni	2	2	6	2	6	8	2												
29 Cu	2	2	6	2	6	10	1												
30 Zn	2	2	6	2	6	10	2												
31 Ga	2	2	6	2	6	10	2	1											
32 Ge	2	2	6	2	6	10	2	2											
—																			
36 Kr	2	2	6	2	6	10	2	6											
37 Rb	2	2	6	2	6	10	2	6			1								
38 Sr	2	2	6	2	6	10	2	6			2								
39 Y	2	2	6	2	6	10	2	6	1		2								
40 Zr	2	2	6	2	6	10	2	6	2		—								
—																			
47 Ag	2	2	6	2	6	10	2	6	10		1								
48 Cd	2	2	6	2	6	10	2	6	10		2								
49 In	2	2	6	2	6	10	2	6	10		2	1							
50 Sn	2	2	6	2	6	10	2	6	10		2	2							
—																			
54 Xe	2	2	6	2	6	10	2	6	10		2	6							
55 Cs	2	2	6	2	6	10	2	6	10		2	6			1				
56 Ba	2	2	6	2	6	10	2	6	10		2	6			2				
57 La	2	2	6	2	6	10	2	6	10		2	6	1		2				
58 Ce	2	2	6	2	6	10	2	6	10	1	2	6	1		2				
59 Pr	2	2	6	2	6	10	2	6	10	2	2	6	1		2				
—																			
72 Hf	2	2	6	2	6	10	2	6	10	14	2	6	2		2				
—																			
79 Au	2	2	6	2	6	10	2	6	10	14	2	6	10		1				
80 Hg	2	2	6	2	6	10	2	6	10	14	2	6	10		2				
81 Tl	2	2	6	2	6	10	2	6	10	14	2	6	10		2	1			
82 Pb	2	2	6	2	6	10	2	6	10	14	2	6	10		2	2			
—																			
86 Rn	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6			
87 —	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		1	
88 Ra	2	2	6	2	6	10	2	6	10	14	2	6	10		2	6		2	
—																			
118 —		2	6	2	6	10	2	6	10	14	2	6	10	14	2	6	10	2	6

for each unit increase in the atomic number. The second element, helium, has two orbital electrons; the third element, lithium, has three electrons; the fourth, beryllium, has four, and so on. But although it can be shown that the two electrons of helium are in the same quantum level (K), the extra electron present in lithium is at a level further from the nucleus. Further electrons, in Be, B, C, etc., are also in this second level (L), and this process of building up the second series of electrons goes on until eight electrons are present in the second level, in neon. The next electron (in sodium, atomic number 11) then enters at the next outer level (M) and the accumulation of electrons proceeds until eight have entered at this level. This maximum is normal for the simpler elements of low atomic number, but those in the third and fourth series of the periodic system can accommodate 18 electrons in the inner level, while the rare earth atoms have 32 electrons as their maximum.

Elements having one electron in the outer orbits belong to the first group of the periodic system (alkali metals), those with two electrons to the second group, and so on.

It can be seen from the table on p. 6 that the building up of outer layers sometimes begins when the inner layers, as judged by the structure of atoms later in the list, are incomplete. For instance, the N-level begins to be formed in potassium and calcium, and then in scandium the M-level is augmented, a process which continues up to nickel. In such cases the properties of the elements which follow one another tend to be very similar. This can be seen in the eighth group, in the iron, palladium and platinum triads, and especially in the rare earths, in which the increase in the number of electrons takes place in a more deep-seated layer. The classification of the elements put forward by Bohr (see p. 25) incorporates these facts of atomic architecture.

All the inert gases after helium have complete outermost shells of eight electrons. According to Kossel's theory,[1] each atom has the tendency to finish off its outer layer with eight electrons; it can accomplish this by uniting with another atom, when it can either rid itself of the electrons in the incomplete outer layer, or take from the second atom the number required to bring the total of electrons in the outer layer up to eight. The rare gases, whose positions in the periodic system vary by 8, 18, or 32 places, contain their maximum number of electrons and have therefore little inclination to acquire more or to react with other atoms. The alkali metals which follow the rare gases in the periodic table have an electron which they tend to give up in order to take on the character of an inert gas. The giving up of this one electron expresses the univalency of the alkali metals. Conversely, the halogens, for example, which precede the rare gases in the periodic system, have outer layers of seven electrons, and thus

[1] *Ann. Physik.*, 1916, 49, 229.

need to acquire an additional electron to complete their outer layer. For this reason an alkali metal atom can combine with one atom of halogen in such a manner that the metal atom transfers its electron to the halogen atom. The alkali metal atom, by loss of the negatively charged electron, becomes a positive univalent ion; the halogen atom becomes a negative univalent ion, and experiments made by Born[1] show that these ions are already present in the solid compound, and are not formed at the moment of solution. In the same manner an atom of an alkaline earth metal, for example, can unite with an oxygen atom; as the former possesses two electrons in its outer layer and the latter six, the total will complete the unfinished layer. This process of building up complete layers is the basis of the most important form of the valency of the elements, which is considered later (p. 49).

In chemical reactions the energy must be sufficient to displace the outer electrons, because an entire reconstruction of the outer electron rings must be effected. Since the structure of the outer electron rings changes periodically with increase in the number of electrons, the chemical properties of the elements will likewise alter periodically with the building up of new shells. The existence of the periodic system of the elements is a result of the periodical changes in their electron layers. Conversely stated, all the properties which are conditional on the envelope of electrons are periodic, and the properties dependent on the atomic nuclei are aperiodic. The latter also differ from the former class, because forces of an altogether higher order are needed to make an alteration in them (see Chap. III).

Atomic Numbers.—If Röntgen rays are directed on an element in a particular way a spectrum is obtained. While the optical spectra vary according to the element, the X-ray spectrum has always the same number of lines and remains unaltered in type although the spectral range changes. The simplest part of this spectrum is the so-called "K" spectrum, consisting of three sharply defined double lines. This, in the shorter wave-length part of the spectrum, is followed by lines of greater wave-length, the "L" series, which has more lines, and only comes within range of observation in the heavier elements—zinc and the elements following it in the periodic system. In the heavy elements from gold onwards, the longest wave-lengths—the seven-lined 'M' series—are visible. It has not yet been possible to photograph the X-ray spectra of the first ten elements, for the wave-lengths of these elements are so great that they almost fall within the range of the visible spectrum; but there is no reason for supposing that these spectra are essentially different from those of the other series.

Moseley,[2] in 1914, discovered the important fact that the square

[1] *Verh. Deutsch. Phys. Gesell.*, 1918, 20, 210.
[2] *Phil. Mag.*, 1914, 27, 703.

root of the vibration frequency of the lines of the "K" spectra is related to the number of the position of the element in the periodic table by a linear law. If the elements in the periodic series are numbered in order, the vibrations are found to vary with the atomic numbers, and not by a periodic increase or decrease. Fig. 2 shows the position of the "K" series in relation to the atomic numbers and Fig. 3 their position with regard to the atomic weight of the element. There can be no doubt that here the atomic numbers are the more important.
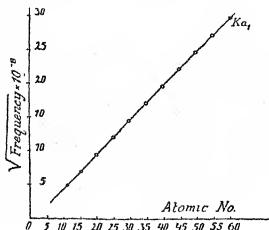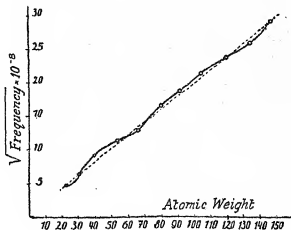
FIG. 2.   FIG. 3.

There is always the same difference between the square root of the frequency of one element and that of the next higher element in the periodic series:

$$\sqrt{V_{Ho}} - \sqrt{V_{li}} = \sqrt{V_{Mg}} - \sqrt{V_{Na}} = \sqrt{V_{Pt}} - \sqrt{V_{Ir}}, \text{ etc.}$$

There is reason to believe (*cf.* Chap. III) that the Röntgen spectra are caused by the electrons of the inner layers; the first line of the "K" series by the jump from the second to the first level, the second line by the jump from the third level to the first, and so on. Now these inner rings are under the powerful influence of the positive charge of the nucleus, while the outer electrons, which cause the optical spectra, are affected by a much smaller electric force. It may therefore be assumed that the regular increase of the square root of the wave-length in passing from one atomic number to the next has its origin in the regular increase of the nuclear charge. In other words, in passing from one element to the next in the periodic table, the nuclear charges increase at the same rate as the atomic numbers. If the charge on the nucleus of an element whose atomic number is 1 (hydrogen) is taken as unity, the number of nuclear charges is the same as the atomic number of an element in the periodic system.

Structure of the Nucleus.—The atomic nucleus, though generally an extremely stable system, may be split into smaller fragments if energies of sufficient magnitude are employed. Such large energies accompany

the emission of α-particles from certain radioactive bodies. Reference to Chapter III will show that the study of radioactivity has led to the discovery of other particles which are similarly effective in the disintegration of atomic nuclei. The following account contains examples of some of these particles, fuller details of which will be found in the section on Radioactivity (pp. 63 ff.).

In 1919 Rutherford found that if nitrogen, whether in the form of the gas or of the solid nitride of sodium, boron, titanium, etc., was bombarded by the fast α-particles emitted by Radium-C (p. 84), a nuclear reaction occurred involving the disappearance of an α-particle and the simultaneous formation of an energetic proton and an oxygen nucleus of mass 17. The proton may be regarded as a hydrogen atom bereft of its electron, the nuclear reaction being formulated

$$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H.$$
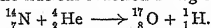
In this equation the subscripts and superscripts represent atomic numbers and mass numbers (nuclear weights) respectively, and their respective sums must be the same for both sides of the equation. It should be noted that the atomic number is implied by the chemical symbol, so that the reaction may be written

$$^{14}N + ^{4}He \longrightarrow ^{17}O + ^{1}H$$

or still more concisely

$$^{14}N(\alpha, p)^{17}O$$

where α and p represent the α-particle ($^{4}_{2}He$) and the proton ($^{1}_{1}H$) respectively. Such a reaction is called an (α, p) reaction.

A similar nuclear reaction involving beryllium gives rise to neutral particles of unit mass, known as neutrons:

$$^{9}_{4}Be + ^{4}_{2}He \longrightarrow ^{12}_{6}C + ^{1}_{0}n \quad \text{or } ^{9}Be(\alpha, n)^{12}C.$$
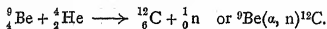
α-particles, protons, neutrons, and also deuterons (which are "heavy protons," represented by $^{2}_{1}D$ or $^{2}_{1}H$ and corresponding to deuterium) may be used as projectiles to effect nuclear disintegrations (see Chapter III). In addition to these massive particles, certain metastable nuclei emit electrons or positrons, the latter being particles of mass equal to that of the electron but bearing unit positive charge; these are also known as positive electrons.

From the above it is clear that the nucleus is a composite body, and while it was once considered to contain enough protons to account for the mass, together with sufficient electrons to reduce the positive charge to the atomic number, it is now believed to consist solely of protons and neutrons, the latter acting as neutral units of mass. The helium nucleus, for instance, which has mass number 4 and atomic number 2, is regarded as being made up of two protons and two neutrons, and not four protons and two electrons.

Theory of Nuclear Forces.—If the nucleus consists of protons and

neutrons the problem arises as to why it is so stable. Electrical forces would be repulsive between proton and proton and inactive between proton and neutron and between neutron and neutron, while the magnetic forces resulting from proton and neutron spin are too small to account satisfactorily for the stability of the nucleus. It becomes necessary, therefore, to postulate the existence of "nuclear forces." The origin and mode of action of these forces is by no means clear, but Yukawa has developed a relatively complete theory on the basis of the interactions between the fundamental particles, observed in experiments on the scattering of neutrons and protons by protons. These observations indicate that the nuclear forces are active over a distance of about 3×10^{-13} cm. only, and according to Yukawa, are transmitted by a field. Calculations show that this field would be expected from particles of mass about 120 times that of the electron and bearing unit positive or negative charge. The discovery of a particle called the mesotron or meson in cosmic rays having such properties appeared to substantiate the theory, but a more rigorous mathematical treatment of the meson field indicates a much greater mass for this particle.

Other theories regard the nuclear forces as exchange forces, analogous to valence forces in the electron shells, and attempt a quantum mechanical treatment along the lines followed in the elucidation of the nature of the chemical bond.

No theory can be considered complete as yet, either in regard to its ability to explain observed facts or in the experimental verification of its predictions. A full review of the present state of our knowledge will be found in the Annual Reports of the Chemical Society for 1938 and 1939.

2. The Structure of Molecules

There is no single simple way in which atoms unite to form molecules, but in every case there is an electrostatic attraction between the components which make up the molecule. The electron layer is the factor on which depends the kind of compound formed when atoms unite, and it is possible to distinguish different extreme types of compounds according to the mechanism of formation. These classes are :—

    1. Polar or electrovalency compounds.
    2. Non-polar or covalency compounds.
    3. Co-ordinate valency compounds.
    4. Odd electron valency compounds.
    5. Field valency compounds.

There are naturally intermediate stages between these main classes (see).

The *polar compounds* are made up of components of opposite charge—or *ions*—that is, of atoms or groups of atoms which have taken up electrons or surrendered them. If the number of electrons in the outer layer of the atom is indicated by a superior index, the formation of sodium chloride from its atoms is shown thus: $Na^1 + Cl^7 = \{Na^0 + Cl^8\}$. The chlorine has become negatively charged by the transfer of an electron from the sodium atom, and the sodium atom positively charged. The sodium atom which has lost one electron is the sodium ion; the extra-nuclear electron shell is identical with that of neon, but the nucleus carries one more positive charge than does the neon nucleus. Similarly, in the case of the chlorine ion, the electron shell is identical with that of argon, but the nuclear charge is one less than that of argon. The two oppositely charged ions form the molecule. The following reactions proceed along the same lines:—

$$Ca^2 + O^6 = \{Ca^0 + O^8\}; \quad Al^3 + N^5 = \{Al^0 + N^8\}; \quad 2K^1 + S^6 = \{2K^0 + S^8\}.$$
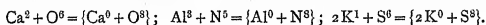
The tendency to form an electron layer like that of the nearest inert gas is to be seen in all these examples; the atom which surrenders electrons forms the shell of the next lower, while the one which takes up electrons forms that of the next higher rare gas.

There is a greater tendency to give up electrons rather than to acquire them, since the collection of similarly charged particles already present tends to repel the latest arrival. Further, Sir J. J. Thomson has shown mathematically that in the lighter elements the presence of more than eight electrons in the outer layer is not possible, owing to this mutual repulsion. This tendency to lose electrons leads to the existence of many more positive than negative ions of elements.

It is often possible for a group of atoms to take up electrons where the single atoms cannot easily do so, and hence negative radicles containing several atoms are common. These are discussed later.

Non-polar compounds are not made up of oppositely charged components, but they also result from the tendency to form an outer layer of eight electrons. In binary compounds of this type this effect is brought about by some of the electrons being common to two atoms. Thus two hydrogen atoms form a molecule in which the two electrons are affected by both nuclei. If the electrons are indicated by dots, this can be expressed thus, $H \cdot + H \cdot = H : H$. Each hydrogen nucleus is in contact with two electrons, so each has a helium shell. Naturally it is not to be supposed that the electrons are in a stationary position between the nuclei; the indication of the electrons by dots between the two H atoms is not intended to show a permanent localisation.

If the movements of the electrons are borne in mind, it is feasible to represent the layer of eight electrons by a cubic atom, that is, to place the eight electrons in the completed layer at the corners of a cube.

While the conception of polar valency was being developed by Kossel, the idea of non-polar valency on the basis of the cubic atom was developed by Lewis,[1] and later by Langmuir.[2]   According to Lewis, the electron configurations in the outer layers of the atoms of the first series of the periodic system can be shown diagrammatically, as in Fig. 4.

Li · Be B C

N O F Ne
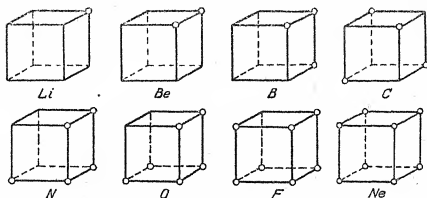
Fig. 4.—Cubic configuration of outer electrons.

Here the tendency to form a complete layer of eight, called an *octet* in this theory, results in the formation of compounds.   For instance, a comparison with Fig. 5 indicates how the fluorine molecule is formed by the two cubes, each of which has one corner vacant, coming together so that they have an edge in common.   By so doing each completes its octet.   In a similar way, in Fig. 6, the oxygen molecule is formed by the cubes having one face in common, as each lacks two electrons.   The rigidity of the structure, it must be remembered, is quite imaginary and bears no relation to the chemical stability.   Representations by means of cubic models are now only of historical interest, for compounds containing triple bonds cannot be represented by this method.   These models were, however, useful in developing the idea of octet shells acquired by *transference* of electrons in the case of electrovalent or polar compounds and of *sharing* of electrons in the case of covalent or non-polar compounds.
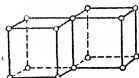
Fig. 5.—Fluorine molecule.   Fig. 6.—Oxygen molecule.
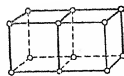
A more convenient notation is to surround the symbol of the atom with dots to the number of the outer electrons, those electrons which are held in common by two atoms (covalent) being indicated by dots placed between the atoms.   The above diagrams then become :—

$$: \ddot{\text{F}} \cdot \ + \ . \ddot{\text{F}} : \ = \ : \ddot{\text{F}} : \ddot{\text{F}} : \qquad : \ddot{\text{O}} : \ + \ : \ddot{\text{O}} : \ = \ : \ddot{\text{O}} :: \ddot{\text{O}} :$$

[1] *J. Amer. Chem. Soc.*, 1916, 38, 762.
[2] *Ibid.*, 1919, 41, 868, 1543 ; 1920, 42, 274.

The distribution of electrons in the oxygen molecule is probably not symmetrical, for this element is paramagnetic. It is probable that the oxygen atoms are linked by one covalent bond and two three-electron bonds : O ⋮⋮ O : (see p. 56).

The intermediate form between polar and non-polar compounds is obviously attained when electrons are present which belong more to one atom than to the other. The most ideal non-polar molecules are those of the elements, which are formed of two or more completely similar atoms. The electrons might then be represented diagrammatically as shared equally between the two atoms as follows ———⋮———. But if a complete transference of electrons has taken place, this could be shown ————⋮, and the polar compound carries charges $+$ $-$. If a smaller shift takes place, namely ———⋮—, there is a smaller charge, but a definite dipole $\delta+$ $\delta-$ is present, the moment of which can be measured by suitable methods.

In compounds containing non-polar or covalent links, two electrons constitute the bond, one being contributed by each of the two atoms which are united. If both electrons are contributed by the same atom, a co-ordinate or semi-polar bond is formed (see p. 51). Compounds containing an odd number of electrons in the linkage are considered in Chapter II, and co-ordination and field valency compounds are dealt with in Chapters XI and XII, and many examples of each kind will be met with throughout the book.

In *field valency compounds* an even weaker force exerted by the nucleus on the electrons is operative, and all of them are formed owing to the bipolar nature of the components of the original compounds. As every chemical unit of structure has positive and negative portions, it is surrounded by electric fields in the same way as a magnet with its two poles is surrounded by a magnetic field. Hence these units attract one another thus :—
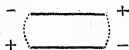
When the units are similar, the product is called a polymer ; when they are different, it is a complex or addition compound. In addition to a polar effect, a geometrical effect must also be operative, so that a stable spatial distribution may result in the crystal.

The partial ionic character of **non-polar** bonds and the partial covalent character of polar bonds, as interpreted in terms of resonance, as well as the metallic bond, are discussed in Chapter II.

3. The Structure of Crystals

Crystals are formed when the forces of valency act in a stationary fashion from one molecule to another. Even the vapours of monatomic elements such as the inert gases or the metals tend to solidify at

suitable temperatures and so to deposit a great number of atoms in a regular manner. These atoms are held together by what are called "Van der Waals" forces, that is by the attraction due to electric fields acting in the same way as "field valency." When the crystal is composed of ions, the ordinary electrostatic forces are in action in accordance with Coulomb's Law. All crystals must be regarded as huge molecules, of which the size is only limited by the capacity for growth of the crystal. It is only in recent years that the structure of crystals has been elucidated.

It happens that the distance between the atoms in crystals is such that the atom layers can act as a diffraction grating for Röntgen rays. This was first suggested by v. Laue, and experimentally verified by Friedrich and Knipping.[1] When a beam of "white" X-rays passes through a crystal slice in the correct position, the diffraction caused by its passage through the atoms gives a pattern of spots on a photographic plate placed in the path of the diffracted light. From the positions of the spots it is possible to calculate the positions of the atoms which have caused the diffraction. Laue X-ray diagrams, taken in different planes of symmetry, differ from one another, and it is possible to see from the symmetry of the points whether the photograph was taken, say, in the direction of a 3-fold or of a

FIG. 7.—Debye and Scherrer's method.

4-fold axis of symmetry. Sir W. H. Bragg and W. L. Bragg have made use of the reflection of monochromatic X-rays at a crystal face; the interference between rays reflected from the layers of atoms lying below the surface gives a kind of point spectrum which can also be

FIG. 8.—Debye and Scherrer diagram for copper.

recorded on the photographic plate,[2] or made obvious by different ionising action.

[1] *Sitzungsber. Bayr. Akad.*, 1912, 305.

[2] For details and a general account of the use of X-rays in determining crystal structure, see *The Crystalline State*, vol. i., by Sir W. H. Bragg and W. L. Bragg, 1933. A summary of the crystal structure of elements and compounds is given on pp. 883-8 of the present work.

When light of one wave-length is used (" pure " X-rays) it is only by accident that the distance between the planes of the lattice is such as to be most effective in producing interference ; but the best conditions can be attained if the angle of incidence of the light on the face of the
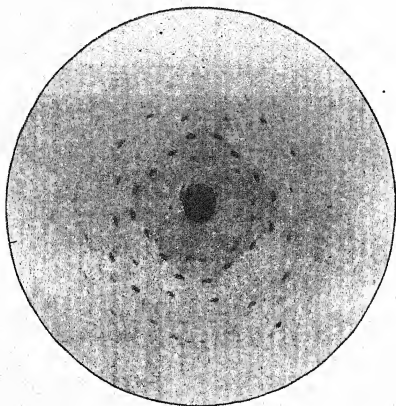
FIG. 9.—Laue diagram for zinc blende.

crystal is increased. The distance the light has to travel between successive layers of atoms becomes greater as the incidence becomes more oblique. In practice the result is obtained by slowly rotating the crystal, the direction of the beam of X-rays remaining unaltered. A photographic image is obtained only when a certain limiting angle of incidence is reached. If the complete rotation is carried out a single

FIG. 10.—Layer line diagram for aluminium nitride.

record is obtained, from which the structure of the crystal can be deduced. In this way "layer line" diagrams (Fig. 10) are obtained, showing not only the reflections due to the equatorial plane, but also those due to planes inclined to the axis of rotation (Schiebold).
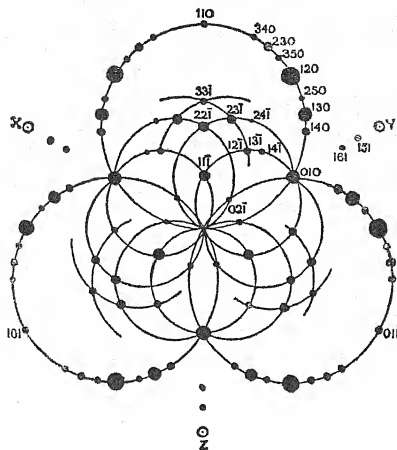
FIG. 11.—Projection of the diamond diagram.
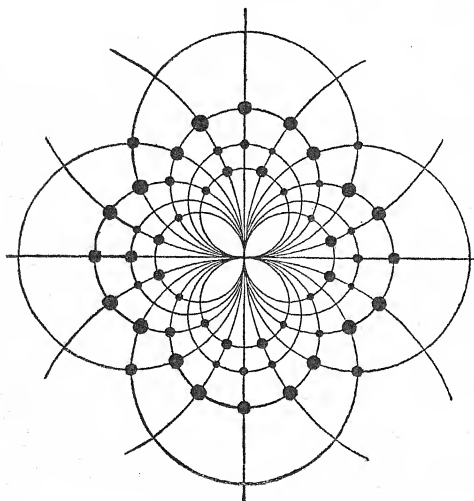
The rotation of the crystal can be avoided if a very large number of crystals is taken instead of a single one; then at least one crystal will be in the appropriate position for reflecting the X-rays to the best advantage. Thus Debye and Scherrer[1] and Hull[2] used very finely powdered crystals, which when traversed by monochromatic X-rays give diffraction by reflection from the innumerable faces in the crystal powder. The diffracted light is recorded on a cylindrical film which surrounds the powder, when a series of circular curves is obtained. This method has the great advantage that it is not necessary to have well-formed crystals, and adjustment of their position is obviated. It can therefore be used when good crystals are unobtainable, and can also be used to find out whether a substance is really amorphous or crystalline. The Debye-Scherrer diagram is obtained only when crystalline forms are present, and so is useful for the exploration of the state of matter in which the orientation of the particles is doubtful. The most useful applications of this method have been in the investigation of colloids, rubber, textile fibres, and other substances which were not formerly considered to be crystalline.

Fig. 7 shows the image obtained on such a film from the powdered crystals in the centre, while Fig. 8 gives the appearance of the same film when unrolled. Fig. 9 is a Laue photograph of the structure of zinc blende with three-fold symmetry. Fig. 10 is an example of a photograph by the layer line method.

Fig. 11 gives the stereographic projection of a Laue photograph for diamond on the three-fold axis, in which the marks on the photograph are represented by dots of varying sizes, showing their positions on the different circles which intersect those made by the diffraction marks reflected from the planes of a zone in the crystal. By means of these projections the positions the individual atoms in a crystal can be calculated. Fig. 12 shows a similar projection from the photograph of rock-salt crystal, which has a simpler structure, with four axes of symmetry.

Crystal Structure of the Elements.— The space lattices in the crystals of elements will now be considered. In many metals[3] this lattice is formed in such a way that the eight corners of a cube and the centres of the six faces are occupied by atoms. A unit of such a face-centred crystal which contains no

FIG. 13.—Face-centred cubic lattice.

metal atoms in its interior will thus have 14 metal atoms on its outer
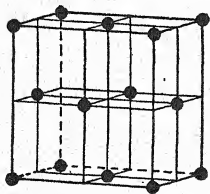
[1] *Physikal. Zeitschr.*, 1916, **17**, 277 ; 1917, **18**, 291.

[2] *Phys. Rev.*, 1917 (ii), **9**, 84 ; **10**, 661, etc.

[3] See Rinne, *Z. anorg. Chem.*, 1916, **96**, 317 ; and Tammann, *ibid.*, 1919, **107**, 96.

planes (Fig. 13). A solid constructed of cubes in this way is completely symmetrical, and hence it is not surprising that this symmetry is characteristic of and present in the majority of metals and is visible in the outward form of the crystal. When this symmetry does not occur, it is because a single atom has to fulfil various functions, the molecule of the metal being thus polyatomic.
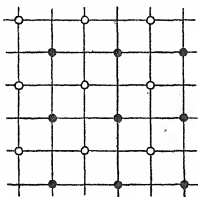
FIG. 14.
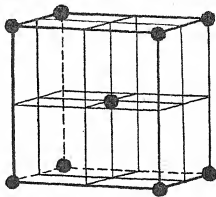
FIG. 15.—Body-centred cubic lattice.

The positions of all the atoms in the space lattice of the monatomic metals can be regarded as identical, although individual atoms may occupy the corners of the cube and others the centres of the faces; the latter form other cubes in which they take the corner positions, while the atoms which were formerly in the corners change into the centre positions. This can be seen from Fig. 14, which represents the front plane only of a combination of cubes. The atoms indicated by circles in one series hold the central positions; in the other series they are seen to be in the corners.

The lattice shown in Fig. 13 is called a *face-centred cubic lattice*, because there is one atom in the middle of each face of the cube.
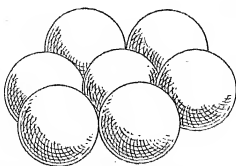
FIG. 16.—Hexagonal close packing.
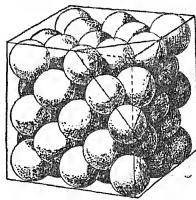
FIG. 17.—Cubic close packing.

Closely related to this is the *body-centred cubic lattice* (Fig. 15), in which the centres of the faces are free from atoms, but one atom occupies the middle point of the cube.

A third arrangement of atoms which is very common in elements is the *hexagonal* arrangement—that of closest packing of spheres. This

structure occurs when the atoms are arranged in suitable layers, as in Fig 16, and the crystals formed from it belong to the hexagonal system. These lamellæ can also lead to face-centred cubic arrangements, and when closest packing does not take place may be arranged in other ways. In close packing, however, the spheres of one layer fit into the hollows in the layers above and below. Fig. 17 shows the development of a face-centred cubic lattice by close packing of spheres.

Most of the metals have one of these three simple structures, as can be seen from the following table, in which the length of edge of the unit cube (a_w) or of the edge and axis of the hexagon (a and c) are given.

Crystal Structure of Metals

Metals with face-centred cubic lattices :

	Sr	Ca	Ce—β	Th	Pb	Ag	Au	Al	Pt	Pd	Rh	Ir	Fe—γ	Cu	Co	Ni	
a_w	6·075	5·56	5·12	5·04	4·92	4·08	4·07	4·04	3·93	3·86	3·82	3·63	3·60	3·55	3·54	cm.$^{-8}$

Metals with body-centred cubic lattices :

	Cs	Rb	K	Na	Li	Nb	Ta	W	Mo	V	Fe—δ	Fe—β	Cr	Fe—α	
a_w	6·05	5·62	5·20	4·30	3·50	3·31	3·27	3·15	3·14	3·04	2·93	2·90	2·88	2·86	cm.$^{-8}$

Metals with hexagonal structure (densest packing) :

	La	Pr	Ce—α	Ho	Hf	Zr	Mg	Ti	Cd	Re	Os	Ru	Zn	Co—α	Be	
a	3·75	3·657	3·65	3·48	3·32	3·23	3·20	2·97	2·972	2·765	2·714	2·686	2·658	2·514	2·29	cm.$^{-8}$
c	6·06	5·924	5·96	3·557	5·46	5·14	5·23	4·72	5·60	4·470	4·32	4·272	4·94	4·11	3·62	,,

The various modifications in which the metallic elements exist differ one from another in the arrangement of the atoms. In iron, the Röntgen spectra give the following results : pure iron stable at ordinary temperatures (α-iron), has a cubic body-centred space lattice in which the length of edge of the elementary cube is 2.86×10^{-8} cm. The disposition of the atoms in this lattice can, however, change with the temperature, and γ-iron, stable at 1000°, has a lattice constructed of cubes which have atoms at each corner and one in the centre of each face (face-centred cube). It is interesting to note that the addition of 3·5 per cent. of silicon to the iron has no effect on the arrangement of the atoms, and, further, that β-iron, which was thought to be a special form of iron, shows at 800°-830° a similar structure to that of the α-iron.

Subdivision by the most delicate mechanical means produces no change in the arrangement of the atoms in metals. Röntgen photographs have shown that the space lattice of colloidal gold does not differ essentially from that of solid gold crystals.

Metals which are not far removed from non-metals in their properties are not so symmetrical in structure and therefore do not belong to the regular system. The most important of these metals are anti-

mony, bismuth, indium, tin and germanium. The lattices of trigonal antimony and bismuth can be taken to be formed by the displacement of a cubic face-centred lattice, thus giving rhombohedra. Tetragonal indium and white tin have structures formed by stretching a face-centred cubic lattice in two directions, with suppression of the atoms lying in the third face. Grey tin and germanium have the diamond structure described below.
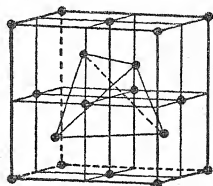
FIG. 18—Diamond lattice.

Symmetrical crystal structure is, however, by no means confined to metals—it is also found in the non-metals. For example, the solid inert gases have face-centred cubic lattices:

	A	Kr	Xe	
a_w	5·42	5·69	6·24	cm.$^{-8}$

Carbon, in the form of diamond, has a lattice of which the outside exactly resembles that of copper (see Fig. 18), but which differs from it in having its interior filled with atoms—in the centre of every alternate cell is a single atom of carbon; these interior atoms form the corners of the tetrahedron inscribed within the cube (see Fig. 18). As a result of this symmetry, it is not surprising that the diamond also crystallises in the regular system. This high grade of symmetry does not exist in other forms of carbon, e.g. graphite (Fig. 19). In this form the atoms of carbon lie in even layers, one over the other, thus giving the flaky structure characteristic of graphite. The hexagons are not piled vertically one on the other in these planes, but are arranged in such a way that a corner of the second hexagon rests perpendicularly over the centre of the first; a third layer lies in a similar position to

FIG. 19.

the first, and the fourth like the second. Thus the sphere of influence of a carbon atom will not be symmetrical, particularly as the

distance between carbon atoms [1] situated on the same plane is only 1.45×10^{-8} cm., whereas the distance between the horizontal planes is 3.41×10^{-8} cm. The connection between atoms lying in the same plane is truly non-polar, while that between those lying in different planes is of the "metallic" type.

The diamond and graphite lattices are not really so different as might appear from the diagrams. By merely squeezing the graphite lattice the atoms can be brought into the positions occupied in the diamond lattice.

The crystal structure of silicon is of the same form as that of the diamond. Rhombic sulphur has a face-centred structure containing 16 atoms per unit cell, probably made up of molecules containing two, four, or eight atoms.

Germanium and grey tin have the diamond structure. The dimensions of unit cube for the elements of Group IV are as follows :

	Diamond.	Silicon.	Germanium.	Grey Tin.	
a_{10}	3·55	5·42	5·63	6·46	cm.$^{-8}$

The force which holds together the atoms in a crystal is identical with that which unites the atoms in molecules in general (as explained on p. 14) and is electrostatic in nature. In electrovalency compounds the lattice points in the crystals are occupied, not by atoms, but by ions.[2] It was difficult to see for some time why these ions, being oppositely charged, did not neutralise one another; but a consideration of the structure of the atom soon makes this clear. The outer layers of the ions are built up of negative electrons only, and although the ions as a whole attract each other owing to their opposite charges, if they approach very near to one another the local repulsion of the outer layers will neutralise the general attraction of the ions. It is possible to calculate the distance at which this effect will take place and to check the calculation by the known compressibility of the crystals. The result of the calculation agrees with the experimental figures if the hypothesis of the cubic atom (p. 13) is adopted.

The application of these conceptions to the field valency compounds which exist in the crystals of elements, and to covalency compounds, is obvious. For a summary of the crystal structure of elements and compounds, see p. 883.

4. Electron Diffraction

Electrons can behave as waves [3] very much like X-rays ; they can thus be scattered and show diffraction patterns similar to those observed

[1] Debye and Scherrer, *Physikal. Zeitschr.*, 1917, **18**, 291.

[2] *Ibid.*, 1918, **19**, 474.

[3] Davisson and Germer, *Nature*, 1927, **119**, 558 ; G. P. Thomson, *Proc. Roy. Soc.*, 1928, [A], **117**, 600 ; **119**, 651.

in the use of X-rays. The wave-length of the electron waves is given by $\lambda = \sqrt{150/V} \times 10^{-8}$ cm., where V is the difference in potential in volts through which the electrons are accelerated. Thus a voltage of 60,000 corresponds to a wave-length of 0·05 Å. The usual wave-length of X-rays is about 1 Å, and the diffraction rings produced are correspondingly wider apart. The rings obtained, using electron beams, although they are closer together are much more intense, and a good diffraction image can be obtained in a much shorter time. It is possible also to photograph many more rings; the apparatus required is comparatively simple, and the material studied is usually in thin films. This method is well suited to the investigation of the structures at the surface of a crystal, owing to the lower penetrating power of electrons. For instance, it has been used to explore the nature of the oxide films on heat tinted nickel and copper, after they have been isolated by anodic corrosion.

Other important information is obtained from electron diffraction in gases and vapours. When a beam of high velocity electrons is passed through the gas at a low pressure and then allowed to fall on to a photographic plate, a central image is caused by the unscattered beam, surrounded by a series of concentric rings of varying intensities, which are disposed in accordance with theoretical predictions. The equations used for such calculations[1] involve the distances and the angles between the centres of the atoms in the molecule. Such measurements, therefore, allow inter-atomic distances and valency-angles to be arrived at. The effective radii in Ångström units of a number of covalently singly-bound elements thus determined are:

C	0·77	.	Si	1·17	.	Ge	1·22	.	Sn	1·40
N	0·70	.	P	1·10	.	As	1·18	.	Sb	1·36
O	0·66	.	S	1·04	.	Se	1·14	.	Te	1·32
F	0·64	.	Cl	0·99	.	Br	1·14	.	I	1·33

Thus the measured bond distance in ICl is 2·31 Å, the additive value from the table, arrived at from results for I_2 and Cl_2, being $1·33 + 0·99 = 2·32$ Å. In many cases the agreement is excellent, but discrepancies are sometimes met with, particularly in fluorine compounds; thus in CF_4, the measured bond distance C—F is 1·36 Å (calc., 1·41) and in OF_2, the distance O—F found is 1·36 and 1·41 (calc. 1·30) and similar anomalies are met with in SF_6, SeF_6 and TeF_6 (see p. 602).

The presence of double bonds brings about a shortening of the bond distances. Thus the value for C=C from electron diffraction measurements is 1·32 Å (compare C—C, 1·54 Å) and for C≡C the distance is 1·22 Å. The importance of these results is considered later in connection with *resonance* (see pp. 53 and 348), which is found also to involve a shortening of inter-atomic distances.

[1] See Glasstone, *Ann. Rep. Chem. Soc.*, 1936, 33, 65-85.

PROPERTIES OF THE ELEMENTS—THE PERIODIC SYSTEM

The Periodic System—Metals and non-metals—Physical properties—
Density and atomic volume—Valency

THE general structure of atoms having been discussed, their other characteristics can now be investigated. In so doing, care must be taken to distinguish between properties which are derived from the nucleus and those which depend on the electron layers. The former change regularly with increase of atomic weight, while the latter undergo a periodic variation (see p. 7). All elements with a complete outer layer have the properties of the rare gases; those with one electron in the outer layer are alkali metals; those with two electrons are alkaline earths. Again, elements which lack only one electron to make up the complete layer—the halogens—have common properties. In accordance with the complete layer of eight electrons in the rare gases of low atomic number, similar elements recur after eight have been passed; while as the higher inert gases have 18 electrons in the inner layers, the similar elements then recur after 18; in the rare earths, with 32 electrons for the complete inner set, after 32 elements.

If the rare gases are placed at the ends of the periods, the first period contains only 2 elements, H and He; the second and third periods contain 8 each, the fourth and fifth 18, and the sixth 32 elements. According to Landé,[1] these numbers, which may be written $2 \cdot 1^2$, $2 \cdot 2^2$, $2 \cdot 3^2$, $2 \cdot 4^2$, have a simple connection with the quantum numbers of the electrons contained in the atoms.

The classification of the elements, introduced by Bohr,[2] is based on these ideas. Hydrogen and helium occupy the first period, and then follow periods of 8, 8, 18, 18, 32 and 5 elements. Elements occupying the same group are connected by vertical or sloping lines. Hydrogen shows connections both with the alkali metals and with the halogens; like the alkali metals it has an outermost shell of one electron and like the halogens, its outermost shell is one electron short of the inert gas structure. Four types of atoms are recognised in this scheme.

(1) Those in which all the electron shells are complete, completion being implied if shells of 8 and 18 are present, even though these are

---

[1] *Naturwiss.*, 1925, 13, 604.
[2] *The Theory of Spectra and Atomic Constitution*, 1924.

less than the maximum possible value of $2n^2$. These elements, the inert gases, have reached an electronic stability which cannot be

Bohr's Classification

```
                    H                           He
                                                2


        Li   Be   B    C    N    O   F   Ne
        3    4    5    6    7    8   9   10


             Na  Mg  Al  Si   P    S   Cl   A
             11  12  13  14  15   16  17   18


K    Ca  Sc  Ti  V   Cr  Mn  Fe  Co  Ni  Cu  Zn  Ga  Ge  As  Se  Br  Kr
19   20  21  22  23  24  25  26  27  28  29  30  31  32  33  34  35  36


Rb   Sr  Y   Zr  Nb  Mo  Ma  Ru  Rh  Pd  Ag  Cd  In  Sn  Sb  Te  I   Xe
37   38  39  40  41  42  43  44  45  46  47  48  49  50  51  52  53  54


Cs   Ba  La  Ce Pr.....Yb Lu  Hf  Ta  W  Re  Os  Ir  Pt  Au  Hg  Tl  Pb  Bi  Po  -   Em
55   56  57  58 59......70 71  72  73  74  75  76  77  78  79  80  81  82  83  84  85  86


-    Ra  Ac  Th  Pa  U
87   88  89  90  91  92
```

increased by additions to or removals from their shells; they, therefore, form no compounds.

(2) Those in which all but the highest quantum group are complete.

These are the elements of the short periods and those of the long periods from seven places before to two places after each inert gas. They are non-transition elements.

(3) These are the first type of transition element and are enclosed in a single frame. They are those elements in which the two outermost electronic shells are incomplete. The term transition element was formerly restricted to those triads with which Bohr's transition groups end, but they are really only the end members of a much longer series. They show variable valency which changes for a given element by single units.

(4) These are the second type of transition element, and are shown in a frame within the first frame. They are those elements in which the three outermost shells are incomplete, and constitute the group of rare earths. In this group, the two outermost electron shells remain largely unaltered in passing from element to element, the addition of electrons taking place in the N level, whereas in this group the outermost level is P. These elements are accordingly even more nearly alike among themselves than are the elements of type (3).

As the conception of atomic number in its relation to the structure of the atom is a recent discovery, Mendeléev and Lothar Meyer arranged the elements in the order of their atomic weights. The series thus obtained shows remarkable periodic variations in many chemical and physical properties. Thus valency, melting point, atomic volume and other properties show a regular variation. If a new series is commenced each time a non-valent element occurs, the result is two short periods, followed by three long periods (of the fourth only the first members are known). A clear survey of the elements is obtained if the first eight members of the long periods are placed vertically under those of the short periods, with the three following members forming a separate group (Group VIII). The remaining elements are placed in further horizontal series, the first member of which originally approaches the first in the vertical group in properties, but shows later on a marked divergence from it. The table (p. 27), originally due to Mendeléev, is thus obtained.

The six elements in each column headed by Roman figures form the chief sub-groups of the system. The smaller sub-groups are formed of three elements of later series, also placed one below the other in these columns.

EXAMPLE.—*Chief Sub-Groups* (1) Rare gases : He, Ne, A, Kr, Xe, Em.
                            (2) Alkali metals : Li, Na, K, Rb, Cs.
                            (3) Alkaline earth metals : Be, Mg, Ca, Sr, Ba, Ra.
                            (4) Halogens : F, Cl, Br, I.
        Minor Sub-Groups   The Elements : Cu, Ag, Au or V, Nb, Ta, etc.

The chemical resemblance between the elements in the major sub-groups, as also in the minor sub-groups, is very remarkable. There is less similarity between those in the various groups taken as a whole. By the above classification of the elements t is easy to obtain a clear general survey of the periodic system, but the more logical

(The figures in heavy type are the atomic numbers, the others the atomic weights)

0.	I.		II.		III.		IV.		V.		VI.		VII.		VIII.
	a	b	a	b	a	b	a	b	a	b	a	b	a	b	
1 H 1.0080															
2 He 4.003	3 Li 6.940		4 Be 9.02		5 B 10.82		6 C 12.010		7 N 14.008		8 O 16.0000		9 F 19.00		
10 Ne 20.183	11 Na 22.997		12 Mg 24.32		13 Al 26.97		14 Si 28.06		15 P 30.98		16 S 32.06		17 Cl 35.457		
18 A 39.944	19 K 39.096	29 Cu 63.57	20 Ca 40.08	30 Zn 65.38	21 Sc 45.1	31 Ga 69.72	22 Ti 47.90	32 Ge 72.60	23 V 50.95	33 As 74.91	24 Cr 52.01	34 Se 78.96	25 Mn 54.93	35 Br 79.916	26 Fe 55.85 · 27 Co 58.94 · 28 Ni 58.69
36 Kr 83.7	37 Rb 85.48	47 Ag 107.880	38 Sr 87.63	48 Cd 112.41	39 Y 88.92	49 In 114.76	40 Zr 91.22	50 Sn 118.70	41 Nb 92.91	51 Sb 121.76	42 Mo 95.95	52 Te 127.61	43 Ma	53 I 126.92	44 Ru 101.7 · 45 Rh 102.91 · 46 Pd 106.7
54 Xe 131.3	55 Cs 132.91	79 Au 197.2	56 Ba 137.36	80 Hg 200.6	57 La 138.92 / 58-71 Ce, etc.*	81 Tl 204.39	72 Hf 178.6	82 Pb 207.21	73 Ta 180.88	83 Bi 209.00	74 W 183.92	84 Po 210.0	75 Re 186.31	85 —	76 Os 190.2 · 77 Ir 193.1 · 78 Pt 195.23
86 Rn 222	87 —		88 Ra 226.05		89 Ac 227		90 Th 232.12		91 Pa 231		92 U 238.07				

* Rare earths: 58 Ce 140.13 · 59 Pr 140.92 · 60 Nd 144.27 · 61 Il · 62 Sa 150.43 · 63 Eu 152.0 · 64 Gd 156.9 · 65 Tb 159.2 · 66 Dy 162.46 · 67 Ho 164.94 · 68 Er 167.2 · 69 Tm 169.4 · 70 Yb 173.04 · 71 Lu 174.99

method would be to arrange them in the form of a spiral, with hydrogen (which is difficult to include in this table in a satisfactory manner) as the centre point: the radii of the spiral are formed by elements belonging to the same vertical series (Johnstone Stoney). This method does not give the gaps in passing from one horizontal series to the next, and possesses several other advantages, which are, however, outweighed by the better general view afforded by the ordinary Periodic Table.

The long period forms of the system (below) may be looked upon as a compromise between the two arrangements, and the break in the series occurs after the rare gases. In this diagram the increasing length of the periods is better shown, especially when the rare earth group is considered. Further, it does away with the need for "sub-groups"; the continuity is more pronounced and the relationships between groups of elements such as Fe, Co, Ni and the Cu, Zn group are emphasised by this arrangement. There are many other advantages of this arrangement, but the long period system is of little value in grouping together elements of the same valency, such as aluminium and the earths or silicon and titanium. Another way of presenting the long period system is given on p. 29.

LONG PERIOD SYSTEM I

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.	14.	15.	16.	17.	18.
Li	Be											B	C	N	O	H	He
Na	Mg											Al	Si	P	S	F	Ne
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Cl	A
Rb	Sr	Y	Zr	Nb	Mo	Ma	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	Br	Kr
Cs	Ba	Rare Earths	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	I	Xe
...	Ra	Ac	Th	Pa	U											...	Nt

To understand the periodic system it is necessary to anticipate the information given in Chap. III, and to realise that many elements consist of a mixture of substances which are chemically identical and only differ from one another in atomic weight (isotopes). The so-called atomic weights are merely the average weights of these mixtures. This is the cause of certain variations from the order of arrangement according to atomic weights. The principal variations are to be found in four different places, i.e.:

	A before K	Co before Ni	Te before I	Th before Pa
Atomic weights .	39·944 39·096	58·94 58·69	127·61 126·92	232·12 231

These variations in order were originally made so that elements having similar chemical properties might appear in the same vertical column. But the fact that the atomic numbers of elements (cf. p. 8) represent their order in the periodic system in the best possible way further justifies this rearrangement. It was formerly thought that the presence of other heavier elements of a different chemical nature was the cause of these deviations, but further research has disproved this; the cause lies in the pleiadic nature of many elements. Moreover, it has been discovered that the atomic weights, as already suggested

Long Period System II

INCREASE IN ELECTRONEGATIVE OR ACIDIGENIC PROPERTIES. →

Series of Period	Type and Number in Series	0	L	II	III	IV	V	VI	VII	VIII	L	II	III	IV	V	VI	VII
1			1 H.														
2	Short 8	2 He	3 Li	4 Be	5 B	6 C	7 N	8 O	9 F								
3	Short 8	10 Ne	11 Na	12 Mg	13 Al	14 Si	15 P	16 S	17 Cl								
4	Long 18	18 A	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe 27 Co 28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br
5	Long 18	36 Kr	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Ma	44 Ru 45 Rh 46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I
6	Very long 32	54 Xe	55 Cs	56 Ba	57 58-71 Ce & La R.E.	72 Hf	73 Ta	74 W	75 Re	76 Os 77 Ir 78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 –
7	Fragment	86 Nt	87 –	88 Ra	89 Ac	90 Th	91 Ux2	92 U									

BASIGENIC PROPERTIES.

← INCREASE IN ELECTROPOSITIVE OR

INSOLUBILITY OF COMPOUNDS ↓

by Prout, are really whole-number multiples of a unit atomic weight, and that deviations occur only through the presence of various isotopic elements which cannot be separated by chemical means (*cf.* Chap. III).

There is yet another reason for the deviation from the whole number in the atomic weights. According to the theory of relativity, the apparent mass of a body is in direct proportion to the amount of energy it contains. Every inactive body (of mass m) represents a quantum of energy, $m \cdot c^2$ (c = the velocity of light). In the atom this energy is exhibited in the movement of the electrons round the atom nucleus and has accordingly an indirect influence on the mass of the atom. Any variation of internal velocity should therefore cause changes in mass, but to come within the range of observation they must be very considerable. Even if we presume that the constituents of every atom are identical and that the negative electrons and positive charges of different atoms vary only in quantity and not in quality, the sum of their masses will not necessarily equal the arithmetical sum of their single constituents. The electrons in the atom are in rapid motion, but their velocity varies with different elements. If the speed were the same in every element, Prout's hypothesis would be justifiable, *i.e.* that the atomic weights are multiples of a certain unit. On account of the variations in velocity it is quite possible that the atom may be composed of multiples of the same unit, but its total weight in the balance does not necessarily represent a multiple of the unit when in motion.

The "mass deficit" in the atom can also be attributed to the building up of the atoms of different elements from protons and electrons, with consequent loss of energy. The "packing fractions," that is, the fractions of mass lost due to this variable diminution in energy, lie on a continuous curve falling from the lighter elements to a minimum in the iron group. The latter are thus the most stable and in all probability their wide distribution in nature is a consequence of this fact.

The Röntgen spectra show that the best method was intuitively arrived at when the elements were arranged in a system which includes the variations mentioned above, instead of in the unaltered order of their atomic weights. In the vibrations of the Röntgen spectral lines any minor variations will disappear (*cf.* p. 8). The atomic numbers remove any doubt as to the arrangement of the system and also indicate gaps which still exist.

From the commencement of the series up to uranium there are a few elements which have not been established with certainty, namely, elements of atomic numbers 43, 61, 85 and 87. Number 43 (Ma) is a higher homologue of manganese (see p. 486), and 61 (Il) is one of the rare earths. That No. 43 was missing was clearly shown by the Röntgen spectra of neighbouring elements; for example, the difference in the root of vibration frequency of molybdenum and ruthenium (atomic numbers 42 and 44) is double that of niobium and molybdenum (41 and 42). The elements derived from the rare earths (57 to 71) could not be included in the periodic system if they were arranged in one group, although the atomic weights of more than a dozen of them are nearly identical and their chemical properties are such that all would come in Groups III or IV of the system. It is very interesting to find that each of these elements has a different X-ray

frequency, the square root of which differs by a constant amount from that of the next element. Each element in this group has thus an individual atomic number; between neodymium (60) and samarium (62) the difference of the root of the vibration frequency is equal to twice the normal value; and here the missing rare-earth element has been indicated. It has been produced by bombarding Nd (60) with deuterons or Pr (62) with α-particles (cf. p. 86).

Elements Nos. 85 and 87 are claimed to have been detected by Allison[1] with the aid of a magneto-optic method. He named element 85, the higher homologue of iodine, alabamine (Am) and a solution containing $2 \cdot 5 \times 10^{-6}$ g. was obtained from 40 kilos of monazite; element 87, named virginium (Vi), the homologue of cæsium, occurs in pollucite, and also to the extent of 1 part in 10^8 to 10^{10} in monazite, kainite and samarskite.[2] A repetition of the magneto-optic method by Papish and Shuman[3] afforded negative results. No. 85 has been unsuccessfully sought as a product of radioactive change from actinium $(-2a)$ and from polonium $(-\beta)$, though an isotope, with chemical properties allied to polonium, has been obtained by bombarding bismuth with artificial α-particles.[4] No. 87 appears as a product from actinium $(-a)$. It has the properties of an alkali metal[5] (cf. table facing p. 72).

Metals and Non-metals.—It is customary to divide the elements in the Periodic Table into two main classes—metals and non-metals. This grouping has the effect of crowding the non-metals into the right-hand top corner of the table. In the first two horizontal series there is no objection to this, but in the succeeding series the rule is followed that non-metals only are placed in the sub-groups on the right-hand side of the column, while the chief sub-groups are principally composed of metals. In the vertical groups of the periodic system the metallic properties of the individual members increase with ascending atomic numbers; hence in the seventh group there are five non-metals, in the sixth four, in the fifth and fourth only two each, and further on there are none at all. Those non-metals which are close to the metal zone are found, particularly in the lower series, to possess properties common to metals (Te, I); for instance, tellurium is a conductor of electricity and at the anode goes into solution as Te''''. The capacity for taking up electrons becomes less as the number of electrons already present increases, for the mantle of electrons diminishes the positive electric field due to the nucleus; conversely, the ease of surrender of electrons is increased. Hence the electropositive character of the elements in a given group is usually augmented with increasing atomic weight.

[1] *J. Amer. Chem. Soc.*, 1932, **54**, 613, 616.
[2] Papish and Wainer, *ibid.*, 1931, **53**, 3818.
[3] *Science*, 1934, **79**, 297.
[4] Corson, Mackenzie and Segrè, *Physical Rev.*, 1940, **58** 177.
[5] Perey, *Compt. rend.*, 1939, **208**, 97; *J. Phys. Radium*, 1939, **10**, 435.

The formation of polyatomic molecules in the gaseous state is confined to the non-metals, though these too are split up into atoms at higher temperatures. The vapours of metals may sometimes contain molecules consisting of two atoms, but only in very small quantities. This occurs when the vapours contain ionised atoms as a result of some
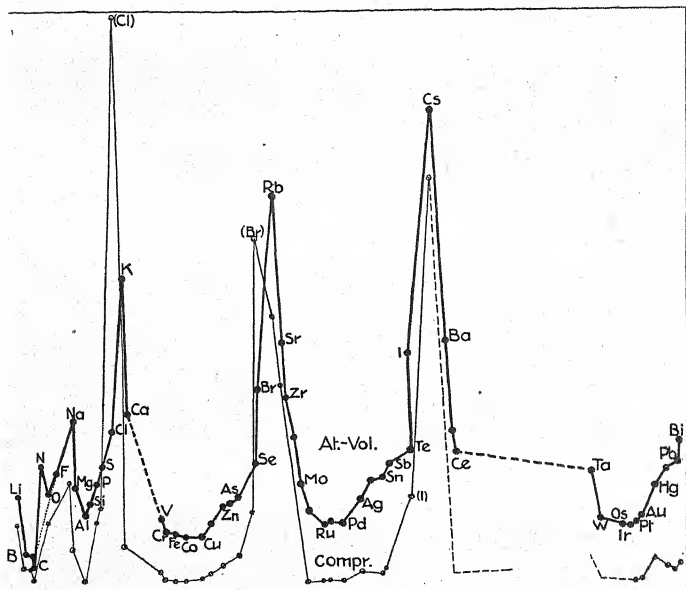
FIG. 20.—Atomic volumes and atomic compressibilities of the elements (after Richards).

stimulus; the atoms are then more prone to combine. Naturally, this effect is most readily observed in the more volatile metals, such as those of the alkalis, mercury and cadmium, in which the presence of diatomic molecules is inferred from the resonance spectra of the vapours. Sodium vapour indicates molecular weights of 24·1 and 25·1 at 705·8° and 570·5° respectively suggesting the presence of some Na_2 molecules.[1]

Periodicity of Physical Properties.—A large number of the physical properties of the elements show periodic changes which

[1] W. H. Rodebush and E. G. Walters, *J. Amer. Chem. Soc.*, 1930, 52, 2654.

correspond with their position in the periodic system. If the atomic numbers are plotted as abscissae and their properties as ordinates, flexed joins are obtained; in several cases the rare gases are the extreme points (melting point, cohesion, etc.), in others the alkali metals (atomic volume, etc.); the halogens occupy the peaks of the plot of compressibility against atomic number (see Fig. 20, p. 32).

Some individual physical properties of chemical elements will now be considered in connection with the periodic system.

Specific Gravity (Density): Atomic Volume. — The specific gravities of. the elements show a marked dependence on their places in the periodic. system. Still more interesting instances of regularity are obtained if, instead of comparing the volumes of equal weights of different elements, we compare the volumes of gram atoms. The atomic volume is proportional to the atomic weight, and inversely proportional to the specific gravity:

$$\text{At. vol.} = \frac{\text{at. weight}}{\text{density}}.$$

Fig. 20 represents the connection between the atomic volumes of different elements and their position in the periodic system. The thick line joins the elements in the order of their atomic numbers. This diagram is highly instructive, and shows a strict adherence to the periodicity found in other properties of elements. The alkalis form the maximum points, while the elements in the middle of a series occupy the minimum points. The sub-groups do not appear as such, but the long periods are each represented by a single loop, so that a minimum occurs in the eighth group, as in the first short period it occurs in Group IV. For this reason the minimum point is sometimes a non-metal (C) or sometimes a metal (Co). The regularity, as shown in this diagram, facilitates the determination by inter- or extra-polation of those atomic volumes and densities which are still unknown.

Such a diagram cannot be absolutely reliable, for many elements exist in several forms, which often possess quite different properties; the choice of the form to be taken as the standard is quite arbitrary. For instance, in diamond and graphite, the former lies very low on the graph, but the latter, with an atomic volume greater than that of beryllium and boron, occupies a normal position. Further, no comparison can be made between liquid and non-liquid elements, as, for example, liquid nitrogen and solid carbon; moreover, the exact values for several solid elements have not yet been accurately determined. Thirdly, any comparison between elements must take place at corresponding temperatures, even though the physical conditions may be identical, for the atomic volumes vary with the temperature. Some elements, for example, show an increase in volume if the temperature is raised above normal, while others remain unaffected; the most favourable temperature for comparison is either absolute zero or the melting point or boiling point. In addition, due consideration must be paid to the fact that elements have different crystal lattices and the distance between the atoms depends on this configuration; again, the molecules of different elements are made up of varying numbers of atoms—for example, metals are monatomic, while sulphur is octatomic. Now, contraction takes place when

C

compounds are formed; polyatomic molecules are combinations of atoms, and therefore it cannot be assumed that the atomic volume of sulphur is equal to one-eighth of its molecular volume.

The effect of such contractions can now be determined by utilising the analysis of crystal structure by means of X-rays. In particular, the work of V. M. Goldschmidt[1] has made it possible to determine the radii of the atoms under comparable conditions. This can be done by comparing only regular face-centred crystals or hexagonal close-packed crystals with one another. The relative positions of the atoms in these two forms are such that comparisons can be made without the factors mentioned above coming into play. Each atom is surrounded by twelve other atoms at equal distances (twelve-coördination). Goldschmidt has found, moreover, that comparisons can also be made on this basis with the volumes in other arrangements of the atoms, for the changes from twelve-coördination to eight-, six-, and four-coördination systems, such as are found in other crystal systems, are accompanied by almost constant contractions in volume—for the first change of 3 to 4 per cent., and for the latter of 11 to 12 per cent.

The atomic volumes of the elements are important in the mechanical arrangement of molecules, for the fitting in of the units is determined by their size. Consequently, the external form of crystals, their hardness, and even the possibility of their formation depends on the volume required by the individual atoms.

The table on pp. 36-37 gives details of the densities, atomic and ionic volumes of the elements, together with other properties which are discussed in the pages which follow.

Ionic Volume.—The volumes of the atoms are naturally altered when they become ions by the accretion or surrender of electrons. As the charge on the nucleus is unaltered when these changes occur, when electrons are given up and a positive ion is formed a contraction takes place, since the attraction of the nucleus for the electrons is now distributed over a smaller number, which are more closely held in consequence. When a negative ion is formed, just the opposite happens and expansion takes place, as the constant electrostatic attraction of the nucleus is now distributed over a greater number. When a positive element has more than one valency, the ionic radius diminishes with increasing valency, as the more electrons are given up the greater becomes the force of the nucleus on the remaining ones. For the opposite reason, when the valency of a negative element increases, the ionic volume becomes greater. The following examples illustrate these changes:

Valency .	4 +	2 +	0	4 −	4 +	0	2 −
Ion .	Pb	Pb	Pb	Pb	Te	Te	Te
Radius .	0·84	1·32	1·74	2·15	0·89	1·33	2·03 × 10⁻⁸ cm.

[1] *Geochemische Verteilungsgesetze, VII. and VIII.*, Oslo, 1926; *Z. physikal. Chem.*, 1928, **133**, 397.

In the structure of solid compounds it is necessary to distinguish between "actual" and "apparent" ionic radius, of which the latter is always the greater. For example, in sodium chloride the "apparent" ionic radius is such that the sum of the radii of the Na and Cl ions is equal to the distance between the centres of these ions in the crystal lattice. From this apparent ionic radius the size of the atom can be deduced in the sense that the crystal is built up of these "spheres of activity," which touch but cannot penetrate one another. In the table on pp. 36-37 are given the atomic volumes, the actual ionic radii,[1] and the apparent ionic radii, which are important for many kinds of crystallographic work. The charges on the ions are shown in brackets.

The variations in ionic radius in the periodic system are shown in Fig. 21 (p. 38), due to Goldschmidt. In the groups, e.g. for Li˙ Na˙ K˙ Rb˙ Cs˙, the radii of positive ions increases with increasing atomic number; the difference between nuclear charge and number of electrons is the same in each group—for the alkalis 1, for the alkaline earths 2, and in consequence the ratio between nuclear charge and total electron charge diminishes and causes a diminution in the electrostatic attraction between the parts of the ions. In the horizontal series, however, the radii of the ions diminish, as, while the nuclear charge is increasing, the number of electrons in the ions remains constant. For instance, Mg, which contains one more electron than sodium in the atomic state, gives up two to become an ion, while the sodium atom gives up only one. Consequently, as the series is traversed, the electrostatic attraction of the nucleus for the electrons is increased.

For negative ions the opposite is true. These ions are formed by the addition of electrons to the neutral atom and in each series, as the nuclear charge increases, the number of added electrons becomes less. In consequence, the ionic volume increases (cf. S, Cl, etc.)

Polarisation and Deformation.—The properties of an atom or ion depend to some extent on the neighbouring atoms or ions. When an atom is in the neighbourhood of an ion it becomes polarised. If the ion is positive, the nucleus of the atom is repelled and the electron layers attracted. The atom thus becomes a dipole and its form is altered.[2] Similarly, non-polar molecules can be polarised by induction of an adjacent charge and also become deformed. Both the polarising action on other molecules or atoms and the effects of polarisation are dependent on the size and charge of the ion, atom or molecule. The larger an ion is, the smaller is its electrostatic attraction for the oppositely charged ion. If the electrostatic action is considered to be concentrated at the middle point of each ion, then the attraction can be calculated according to the inverse square law. Consequently the large iodine ion will exert a smaller force on a potassium ion

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[1] H. Grimm and H. Wolff, Z. physikal. Chem., 1926, 119, 254.

[2] Fajans and Joos, Z. Physik., 1924, 23, 1.

Element	Density	Atomic Volume of the Commonest Form	Atomic Radius (Goldschmidt) in cm $\times 10^{-8}$	Apparent Ionic Radius in cm $\times 10^{-8}$	Actual Ionic Radius in cm $\times 10^{-8}$	Compressibility at 20°$\times 10^{7}$	Coefficient of Cubical Expansion at $\times 10^{6}$	Atomic Frequency $\times 10^{-12}$	Hardness (Moh's Scale)
H solid	0.0763	13.21		1.27(')				7.3	
H (para)	0.088	11.5							
He	0.188	21.3						0.5	
Li	0.59	11.8	1.56	0.78(')		9.0	190	9.65	0.6
Be	1.83	4.9	1.05	0.34(")				21.61	
B	2.45	4.5				0.3			9.5
C Graphite	2.130	5.6	0.77			3.9	7.2	21.0	
C Diamond	3.52	3.4	0.71			very small	0.3	24.0	10.0
N solid	1.026	13.6	0.60		0.87(")			1.9	
O solid	1.4256	11.2		0.60(")	0.74(")			1.3	
F liquid	1.14	16.7		1.33(')	0.61			1.35	
Ne liquid	1.204	16.8						0.26	
Na	0.9066	22.9	1.86	0.98()	0.52()	15.6	21.6	3.92	0.4
Mg	1.74	14.0	1.62	0.78()	0.44()	2.9	7.83	7.76	2.0
Al	2.66	10.2	1.43	0.57()	0.40()	1.47	7.2	7.65	2.9
Si cryst.	2.49	11.4	1.18	0.39(); 1.98(''')	0.36(··)	0.32	2.3	8.47	7.0
P violet	2.34	13.3		0.3–0.4(···)		20.5			
P yellow	1.83	16.9						4.8	
S rhomb.	2.0989	15.3	1.04	0.34(···); 1.74(")	1.8(''')	9.2	18.0	3.88	0.5
S monocl.	1.96	16.3							2.0
Cl liquid	1.66	21.4	1.07	1.81(')	0.95(')	12.9		2.44	
A	1.809	22.1			0.87			1.0	
K	0.863	45.3	2.23	1.33()	0.79()	31.7	25.0	1.52	0.5
Ca	1.545	25.9	2.21	1.06()	0.71()	5.7		4.91	1.5
Sc.		?	1.51	0.83()	0.68()				
Ti.	5.174	9.3	1.49	0.64(); 0.4(···)	0.63()			8.34	
V.	5.737	8.8	1.32	0.65()				8.37	
Cr	7.1	7.7	1.25	0.91(); 0.52()		0.9		2.79	9.0
Mn	7.39	7.4	1.36*	0.83(); 0.67()		0.84	6.2	2.74	
Fe	7.87	7.1	1.27*	0.78()		0.63	3.6	8.25	4.5
Ni	8.9	6.6	1.244*			0.40	4.2	8.07	
Co	8.718	6.8	1.257*	0.82()			3.8	8.13	
Cu	8.933	7.1	1.276*	0.83()	0.66()	0.75	5.0	6.72	3.0
Zn	7.123	9.2	1.374*	0.62()	0.50()	1.7	8.7	4.36	2.5
Ga	5.904	11.8	1.33	0.44(); 0.4(···)	0.53()	2.09	5.5	2.56	1.5
Ge	5.366	13.6	1.394*	0.69(); 0.4(···)			1.6	4.85	6.3
As met.	5.727	14.8	1.26	1.96(')		4.5	11.4	4.53	3.5
Se grey	4.81	16.5	1.13					2.74	3.5
Br liquid	3.187	25.1	1.19		1.16(··)	12.00		1.91	
Kr	3.38	24.5			0.90	52.00		0.70	
Rb	1.52	56.2	2.36	1.49()	0.91()	40.0	27.0	1.18	0.3
Sr	2.60	34.5		1.27()	0.87()			3.03	1.8

	C2	C3	C4	C5	C6	C7	C8	C9	C10
Y	4.57	19.5	…	1.06(VI)	0.83(")	…	…	5.67	…
Zr	6.52	13.97	1.62	0.87(IV)	0.79(")	…	…	7.02	…
Nb	7.37	12.7	1.43	0.69(VI); 0.69(VII)	…	…	1.1	7.27	…
Mo	9.01	10.7	1.36	0.65(IV)	…	0.46	2.88	6.47	6.5
Ru	12.26	8.3	1.322*	0.65(IV)	…	…	2.55	6.44	4.8
Rh	12.1	8.5	1.343*	0.69(IV)	…	0.54	3.8	5.52	…
Pd	11.9	9.0	1.370*	…	…	…	…	…	…
Ag	10.492	10.3	1.442*	1.13(I)	0.74(I)	1.01	5.7	4.36	2.7
Cd	8.648	13.0	1.521*	1.03(I)	0.71(I)	2.1	9.3	2.74	2.0
In	7.421	15.1	1.569*	0.74(I)	0.68(I)	1.9	12.5	2.15	1.2
Sn	7.298	16.3	1.582*	2.15(IV)	…	2.4	6.7	2.28	1.8
Sb	6.618	18.2	1.614*	…	1.24(III)	…	3.3	2.90	3.8
Te	6.235	20.4	1.33	0.89(VI)	1.12(II)	…	5.0	2.45	2.3
I	4.894	25.9	1.36	2.20(I); 0.94(VII)	1.09	13.0	25.0	1.66	0.8
Xe	4.323	30.1	…	…	…	…	…	0.64	…
Cs	1.886	70.4	2.55	1.65(VI)	1.06(VI)	61.0	29.0	0.97	0.2
Ba	3.5	39.0	…	1.43(VI)	1.06(VI)	…	…	2.38	…
La	6.15	22.6	1.83	1.22(VI)	1.04(VI)	…	…	2.1	…
Ce	6.78	20.7	…	1.18(VI); 1.02(IV)	0.98(IV)	…	…	2.0	…
Pr	6.60	21.4	…	1.16(VI); 1.00(IV)	0.91(IV)	…	…	2.2	…
Nd	7.05	20.5	…	1.15(VI)	0.90	…	…	2.1	…
Sa	6.93	21.7	…	1.13(VI)	0.87	…	…	…	…
Eu	5.24	29.00	…	1.13(VI)	0.86	…	…	…	…
Gd	…	…	…	1.11	0.84	…	…	…	…
Tb	8.56	18.97	…	1.09	0.83	…	…	…	…
Dy	…	…	…	1.07	0.82	…	…	…	…
Ho	…	…	…	1.05	0.82	…	…	…	…
Er	…	…	…	1.04	0.81	…	…	…	…
Tm	…	…	…	1.04	0.79	…	…	…	…
Yb	7.01	24.76	…	1.00	0.78	…	…	…	…
Ln (Cp.)	…	…	…	0.99	0.82	…	…	…	…
Hf	13.31	13.42	1.585*	…	…	0.53	…	5.19	…
Ta	16.6	10.9	1.46	0.68(V)	…	0.27	2.3	5.87	…
W	18.72	9.8	1.408	…	…	…	1.1	…	…
Re	21.4	8.8	1.382*	…	…	0.38	…	…	…
Os	22.48	8.5	1.336*	0.67(IV)	…	…	2.0	5.23	7.0
Ir	22.42	8.6	1.352*	0.66(IV)	…	…	1.97	5.03	6.5
Pt	21.4	8.7	1.386*	…	…	…	2.7	4.34	4.3
Au	19.32	10.2	1.439*	1.12(I); 1.95	0.77(III)	0.64	4.29	3.36	2.5
Hg liquid	14.382	13.9	1.55*	1.49(I); 1.05(II)	0.74	3.95	18.2	1.26	1.5
Tl	11.85	17.2	1.707*	1.32(I); 0.84(III); 2.15	0.72	2.3	9.0	1.82	1.2
Pb	11.38	18.2	1.747*	…	…	2.33	7.89	1.81	1.5
Bi	9.781	21.3	1.82*	…	…	3.0	4.03	1.63	2.5
Rn liquid	5.7	39.0	…	…	…	…	…	…	…
Th	12.16	19.2	1.82	1.10(IV)	1.21	…	…	2.4	…
U	18.685	12.8	…	1.00(IV)	1.08	…	…	3.13	…

* Values marked * are for twelve-coördination.

with which it is combined than will the smaller fluorine ion attached
to the same positive ion. The deformation of the metal ion by
the negative ion diminishes with the size of the latter. Conversely,
an ion is itself more deformed by other ions the larger its size,
assuming that the charge is the same. Hence the deformability
increases from fluorine to iodine, or indeed in any group with increasing
atomic weight. Further, the negative ion in a salt is more deformed

FIG. 21.—Actual ionic radii (Goldschmidt).

than the positive, as it carries more electrons and the nucleus thus
attracts the electron shell less forcibly. If, however, the cations of a
series in the periodic system are considered, it will be seen that they
are deformed to a diminishing extent as the atomic weight is increased,
because they are already so contracted owing to the action of the
highly charged nucleus on the smaller number of electrons present.
When a metal cation has different valencies, the ions of higher
valency are obviously less deformable than those of lower valency. In
this sense the chemical action of atoms depends on their total charge
in the first place and on their volume in the second, and a large
number of chemical and physical facts can be explained by taking these
factors into consideration.

It is also revealed that the same element may have different properties in different compounds. The potassium ion in KF is not identical with that in KI, for instance. The polarisation, distortion and alteration in volume of the ion due to the presence of adjacent ions alters its properties ; this often passes unnoticed as the properties of the ion are largely concluded from its behaviour in reaction, when it moves from one set of surroundings to another. In the solid condition, however, the properties of the fundamental units of matter depend on their partners in the compounds.

Hardness.—This property also shows dependence on atomic volume and charge, and consequent periodicity. According to Friederich,[1] hardness is a function of the quotient : $\dfrac{\text{Valency}}{\text{Atomic volume}^{\frac{2}{3}}}$. It is affected by the build of the crystal, and as the electrostatic attraction of the particles is inversely proportional to the square of the distance between their centres and directly proportional to the charges they carry, hardness is greatest for crystals of small atomic volume and high valency. The diamond fulfils these conditions and consequently is high in the scale of hardness. For a further discussion see p. 532.

The Parachor.—The difficulty of choosing a suitable temperature for the comparison of atomic and molecular volumes has already been mentioned. The use of the function known as the parachor represents an attempt to make such a comparison under conditions of equal internal pressure of liquids, but owing to the extreme difficulty of measuring this pressure, the surface tension is used as a quantitative indication of this pressure. The parachor (P) is found from the formula :

$$P = \frac{M}{D-d}\gamma^{\frac{1}{4}}$$

where M is the molecular weight, D and d the densities of the liquid and vapour respectively, and γ the surface tension. This expression has the further advantage of being independent of temperature over wide ranges.

Sugden[2] has determined the parachors for a large number of liquids. It is found that in saturated organic compounds it is an additive function, and once the atomic parachors are found those of other compounds can be calculated and agree with the observed values. In compounds which are unsaturated additions must be made for each particular kind of bonding present. These structural parachors are referred to later (p. 52).

As may be expected, the atomic parachor is a periodic property, and, when plotted against atomic number, gives curves similar to those

[1] *Fortschr. Phys. Chem.*, 1926, **18**, Heft 12.

[2] *The Parachor and Valency*, London, 1930 ; *J. Chem. Soc.*, 1924, **125**, 1177, and later papers

obtained for atomic volume. This can be shown from the values for
the first two short periods:

H	He	Li	Be	B	C	N	O	F
17·1	20·5	(50)	37·8*	16·4	4·8	12·5	20·0	25·0
	Ne	Na	Mg	Al	Si	P	S	Cl
	25·0	(80)	—	38·6*	25·0	37·7	48·2	54·3

(Values in brackets are approximate only ; those marked with * are derived from
few compounds.)

As with atomic volume, the alkali metals are at the peaks, while
Group IV gives the lowest values. In passing from a halogen to
an inert gas there is hardly any change in the parachor, e.g. from
F to Ne and from Cl to A (54·0), and in the transition series the
curve is very flat, e.g. from Ti to Zn (45·3*, 50·7*).

Among the physical properties of the elements, directly related
to their atomic volume, is the **vibration frequency.** The atoms
may possess energy which causes motion in a definite direction ; in
addition they possess an energy of vibration causing them to vibrate
round a central point. The number of oscillations per second is called
the vibration number or atomic frequency. The melting point is the
temperature at which the radii of the vibrations of the atoms become
equal to their respective distances from one another ; they thus arrive
at the extreme points of the space lattice, which were not reached
in the solid state. The atomic frequency can be calculated from this
and other assumptions, making use of the specific heat, density, com-
pressibility or atomic volume of the element.[1] The result of these
different calculations is always the same ; hence it is clear that all these
properties are in intimate relation to each other and vary concurrently.
Thus, for example, the following expressions are proportional to each
other :

$$\frac{1}{\text{compressibility}} ; \quad \frac{\text{abs. melting pt.}}{\text{atomic volume}} ; \quad \frac{\text{spec. heat}}{\text{coeff. of expans.} \times \text{at. vol.}}$$

It is hardly necessary to add that the regularity of the periodic system
shown in the melting point and atomic volume, is also to be found in
the compressibility, atomic frequency, and expansion of the elements, as
well as in all those factors which are influenced by the above properties.
A few examples, e.g. compressibility, expansion, atomic frequency and
hardness, are included in the table on pp. 36-37. A comparison shows
the variation of these properties with the position in the periodic system.
It shows also that elements of the highest atomic volume possess the
greatest compressibility and the highest coefficients of expansion, but
that their atoms show the slowest rate of vibration. It is specially
interesting to investigate the relationship of the properties to one another ;
in many cases it is possible to ascertain their proportionality to other
properties by calculation.

[1] For literature see B. Blom, *Ann. Phys.*, 1913 [4], 42, 1397.

Melting and Boiling Points of the Elements

The upper figure gives the m.pt., the lower (italic) the b.pt.[1]

	0.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1	H −258° / *−253°*	Li 186° / *1370°*	Be 1281° / *—*	B subl. / *—*	C 3800° / *4230°*	N −210.5° / *−195.7°*	O −227° / *−182.8°*	F −233° / *−188°*	
2	Ne −248.8° / *−246.3°*	Na 97.6° / *877°*	Mg 659° / *1107°*	Al 657° / *1800°*	Si 1458° / *arc*	P 44.2° / *287.3°*	S 112.8° / *444.5°*	Cl −102° / *−33.7°*	
3 a	A −189.9° / *−185.8°*	K 62.5° / *757°*	Ca 810° / *1439°*	Sc — / *—*	Ti 1825° / *arc*	V 1680° / *—*	Cr 1830° / *2200°*	Mn 1242° / *1900°*	Fe 1530° / *2450°* Co 1490° Ni 1450° >Mn <Cr
b		Cu 1083° / *2310°*	Zn 420° / *929°*	Ga 29.8° / *1700°*	Ge 900° / *—*	As <800° / *610°*	Se 217°* / *688°*	Br −7.3° / *58.8°*	
4 a	Kr −157° / *−151.7°*	Rb 38.5° / *696°*	Sr 752° / *1366°*	Y 1475° / *—*	Zr 2130° / *—*	Nb 1950° / *—*	Mo 2840° / *diff. arc*	Ma —	Ru >2450° / *arc* Rh 1996° / *arc* Pd 1555° / *arc*
b		Ag 961° / *1955°*	Cd 321° / *770°*	In 155° / *>1450°*	Sn 231.9° / *2270°*	Sb 630° / *1440°*	Te 452° / *1390°*	I 113° / *182.5°*	
5 a	Xe −112° / *−108.6°*	Cs 28° / *670°*	Ba 658° / *1537°*	Rare earths †	Hf ca. 2200° / *—*	Ta 2850° / *—*	W 3660° / *arc*	Re 3170° / *—*	Os 2500° / *arc* Ir 2454° / *arc* Pt 1770° / *arc*
b		Au 1064° / *>2200°*	Hg −39° / *357.2°*	Tl 303° / *1515°*	Pb 327° / *1525°*	Bi 269° / *1420°*			
6	Rn −71° / *−65°*		Ra ca. 700° / *—*		Th >1700° / *—*		U Br. red heat / *>Fe*		

* Metallic form.

† La 810° Ce 623° Pr 940° Nd 840°

arc = in the electric arc.

[1] Some of the values in this table have not yet been finally decided, e.g., Leitgebel (Z. anorg. Chem., 1931, 202, 305) has obtained the following values for boiling points, some of which are widely different from those given above: Mg, 1097°; Zn, 907°; Cd, 767°; Pb, 1740°; Tl, 1457°; Sb, 1635°; Bi, 1500°.

Not all properties, however, show periodicity, as was seen in the frequency of the Röntgen spectral lines (*cf.* p. 8). The **atomic heat** —the product of specific heat of the solid element and its atomic weight—is aperiodic and nearly constant (at room temperature, about 6·4). Thus the quantity of heat which is necessary to cause an equal rise of temperature in the different elements is not a periodic but a linear function of the atomic weight. Atomic heat is dependent on the atomic mass, or, in other words, on the nucleus of the atom, but not on the electron layers. The chief variations from the mean atomic heat, 6·4, occur among elements of low atomic weight, more especially the non-metals :

Element	C	H	B	Be	Si	O	P	S	Ge
Atomic heat	1·8	2·3	2·7	3·7	3·8	4·0	5·4	5·4	5·5

The atomic heat varies with change of temperature, but becomes reasonably constant with temperature when a value of about 6·4 is reached. The study of the atomic heats at low temperatures is very interesting (Nernst's Heat Theorem) ; for further information a text-book on physical chemistry should be consulted.

Melting Points (*cf.* table on page 41). A connection between atomic volume and melting point has already been noted on p. 40. As the process of melting is one of breakdown of the crystal lattices, the melting point will depend on the electrical forces which hold the lattice together. Hence carbon has a high melting point, for the atomic volume is very small so that the electrons lie very close to the nucleus and are heavily attracted to it. The melting point falls in the alkali metal group with increasing atomic weight, as the increasing number of electron layers diminish the attracting power of the nucleus of one atom for the electrons of a second. It is not possible, however, to deal generally with the melting points of the elements, as the actual values are not subject to simple rules.

1. Vertical Groups.—In Groups V, VI, VII, VIII and 0 the melting point rises very regularly with the atomic weight, though the increase is greater the higher the melting point of the element, *e.g.* :

He Group.	F Group.	O Group.	N Group.
from $-271°$ to $-157°$ } $\Delta\ 114°$	$-233°$ $113°$ } $\Delta\ 346°$	$-227°$ $452°$ } $\Delta\ 679°$	$-210°$ $630°$ } $\Delta\ 840°$.

This rise of the melting point also takes place in the minor sub-groups, but in the chief sub-groups I and IV, with an increase in atomic weight, it falls more when the first member of the group has a high melting point :

Li Group.	C Group.
from 186° to 28° } $\Delta\ 158°$	3800° 2130° } $\Delta\ 1670°$.

In the minor sub-groups the variations of the melting points are irregular. Silver, according to its atomic weight, takes a position between copper and gold, but in melting point it ranks beneath them. This effect can be accounted for by the volume relations of the atoms (lanthanide contraction, see p. 424). Variations occur in the chief sub-groups II and III, partly owing to the fact that the top members of these groups show a great similarity to those of the following group (Be with Al, B with Si).

2. Horizontal Series.—In the horizontal series the melting points rise to a maximum at the centre of the table. In the first two periods the fall occurs as a sudden drop between the fourth and fifth groups (from carbon to nitrogen, and from silicon to phosphorus), but in later periods these sudden drops do not occur. In the first period the only exceptions to this rule are phosphorus and sulphur; the latter has a higher melting point than is expected from its place in the system. This is doubtless due to the complexity of the sulphur molecule, so that it is not directly comparable with the elements in its vicinity.

In the later long periods two different maxima in the melting point curve can be distinguished. If the long periods are taken as a whole their centre point will be situated in the eighth group, but if divided in half so that the chief sub-groups and minor sub-groups are treated singly, their centre points will lie respectively in the fourth and fifth groups. Actually, both series of maxima exist; in the third period, at Ti and Ge in the fourth group and again at Ni in the eighth group. The maxima in the fourth and eighth groups appear to merge together in the later periods, meeting in the sixth group at Mo and W. There is then no maximum point in the centre of the half-period at antimony or lead.

Boiling Points.—1. Vertical Groups.—The conditions are similar to those found for the melting points. In the series of rare gases, as well as in Groups V-VIII, including their corresponding sub-groups, the boiling point rises with an increase of atomic weight; in the chief groups of the first and fourth series the fall goes parallel to the increase in atomic weight; in the second and third groups, and also in the minor sub-groups of the earlier groups, the curve is irregular, showing first a rise (Group III), then a fall (Group II), followed by an irregular progress (Group I).

2. The same analogy is found in all the horizontal periods; a maximum in Group IV, a second in the long periods in Group VIII; the boiling points fall steadily in both directions, with a comparatively important jump in the two first periods between C and N and between Si and P. The boiling point of phosphorus is relatively too low in comparison with that of sulphur.

It is not possible, however, to draw a complete parallel between the positions of melting and boiling points; this may be seen by comparing the noticeably slight difference between the two points in the rare gases with the great difference in the case of tin. Moreover, there are some elements whose boiling points, under atmospheric pressure, lie lower

than their melting points—these therefore sublime (boron, arsenic). There is, however, some relation between the two points: in non-metallic groups of the periodic system the difference between melting point and boiling point increases with rising atomic weights, but decreases in the metal groups,[1] as will be seen in the following table. Here the critical temperature is given and not the boiling point under atmospheric pressure, the former being usually 50 per cent. higher than the latter.   The differences between the critical temperature and melting point are as follows:

A	70·5°	Cl	248°	O	109°	N	64·5°
Kr	106·5°	Br	309·5°	S	685°	P	523°
Xe	154·7°	I	398·6°	Se	955°	Sb	1665°
				Te	1767°	Bi	1994°
		Na	1310°	Zn	1111°	Sn	3310°
		K	1201°	Cd	981°	Pb	2096°
		Rb	1142°	Hg	711°		
		Cs	1114°				

The melting and boiling points of carbon are fairly close together; its vapour pressure at the melting point is $\frac{1}{8}$ atm. This element, like the metals, becomes plastic below its melting point. A bar of graphite 5 cm. long and 5 mm. in diameter, heated to a white heat by a current of 800 amps., becomes as pliable as a red-hot iron nail. With further rise of temperature, drops of liquid carbon form at intervals; graphite liquefies in the crater of the electric arc.   The melted product always solidifies into pure graphite.[2]

Appearance.—Metals possess a characteristic metallic lustre, but the non-metals do not, although here, as usual, intermediate stages are found in which certain non-metals have a semi-metallic appearance. These are:

(B)	C	—	—	—
	Si	P	—	—
	—	As	Se	—
	—	[Sb]	Te	I

It will be seen that their position in the periodic system is sharply defined; it begins in the fourth group, the first member of which (C) has a semi-metallic appearance; the member of each succeeding group which first shows this property is seen to be one horizontal row lower.

The non-metals placed on the right-hand side of the table above this diagonal do not show a semi-metallic appearance; they are transparent, and are lighter in colour the higher their position in the respective groups; and the further removed they are from the metals. The variation in a single group is most obvious in the increased

[1] Herz, *Z. Elektrochem.*, 1918, **24**, 48.
[2] Lummer; for literature see Münch, *Z. Elektrochem.*, 1921, **27**, 361, and Ryschkewitsch, *ibid.*, 445.

absorption of light with an increase of atomic weight in the groups F—Cl—Br—I and O—S—Se—Te. On the other hand, the result of comparing colours in the horizontal series must necessarily be incomplete, because both the inner structure of the molecules and the number of their atoms varies from group to group.

All the metals possess a white or grey lustre, with the exception of copper and gold. Silver, which occupies a place between copper and gold does not possess the yellow colour common to both these elements. It is possible, however, to distinguish the non-yellow metals from each other, for they incline either to a reddish colour as in bismuth, or to a bluish colour like lead; even when the difference in colour is less notable it is easy to differentiate, as for example between iron and aluminium, or between silver and the purer white of nickel.

Spectra.—The origin of spectra was described on p. 3 as being vibrations caused by the translation of electrons from one orbit to another; these vibrations take the form of absorption or emission spectra according to the direction in which the electrons are moving. The similarity between the electron rings of elements belonging to the same groups of the periodic system is reflected in the spectra of these elements. For example, all the alkali metals have a spectrum consisting of a small number of lines; the spectra of alkaline earth metals are banded with numerous lines; the spectra of the rare gases show a marked similarity to each other. This is specially noticeable in the arc spectra caused by the collision of slowly moving electrons. On the other hand, the spark spectra resemble the arc spectra of elements belonging to the previous group; for example, those of the alkaline earths resemble the arc spectra of the alkalis. The spark spectra are due to the ionised atoms, which, having given up one electron, resemble in their outer layers the non-ionised atom of the preceding group. Calculations based on spectral lines are of immense importance in developing our knowledge of the structure of atoms and for many other physical investigations (cf. p. 3).

Spectra due to molecules, as distinct from those due to atoms, are also valuable in the solution of many chemical problems. If the energy of a molecule is changed, there may be four effects:

(1) An electron may change its orbit, very much as it does in the production of atomic spectra.

(2) The atoms constituting the molecule may vibrate. This involves a change in inter-atomic distances, and is subject to quantum relationships, just as is (1).

(3) The molecule as a whole may rotate, and this also takes place quantum-wise.

(4) Translation of the molecule may take place, but this is not subject to quantum effects.

The energy changes needed to produce (1), (2) and (3) are in the approximate ratios of 10,000 : 100 : 1. The quantum, $h\nu$, is thus greatest for (1) and least for (3), and ν follows the same order, for h is constant; the spectrum due to (1) falls in the visible or ultra-violet, that of (2) falls in the near infra-red and (3) in the far infra-red.

Theoretically (3) is the simplest, but there are the greatest experimental difficulties in dealing with it. Only molecules possessing a dipole moment give a rotation absorption spectrum, for the rotation of such a molecule causes a change in the electromagnetic (light) field in which it is rotating. Chlorine, for example, does not give such a spectrum, but that of hydrogen chloride consists of a series of lines almost equally spaced. The moment of inertia of the molecule can be calculated from the positions of these lines; if the masses of the two atoms are known, the inter-atomic distances can be arrived at. Alternatively, if the inter-atomic distances have been determined, say from electron diffraction experiments, atomic masses can be computed. For example, $H^{35}Cl$ will rotate more rapidly than $H^{37}Cl$ (see isotopes, p. 73). On account of the experimental difficulties in making precise measurements in the far infra-red, it cannot be determined if the observed shift is that required theoretically. In the vibrational-rotational spectra (see next paragraph) the calculated moments for $^{1}H^{35}Cl$ and $^{1}H^{37}Cl$ are found to agree with the experimental results. Also, after the discovery of heavy hydrogen, a careful examination of the band spectra revealed the presence of $^{2}H^{35}Cl$ and $^{2}H^{37}Cl$. Isotopes of nitrogen, oxygen and carbon (see p. 77) were first detected by this method.

It is much easier to observe (2) accurately, but these spectra are complicated by a change of rotational as well as vibrational energy, so that rotation-vibration spectra result. There is a set of vibrational sub-levels associated with each electronic level, and every vibrational level has a set of rotational sub-levels. The rotational lines are close together, and under low spectroscopic resolution appear as a continuous absorption band. The distance between these lines, forming the fine structure of the band, is due to a difference of one quantum of rotational energy, and is the same as in the far infra-red spectrum. Moments can be calculated from the positions of the lines, and the force opposing the vibration of the molecule can also be calculated. This gives a measure of the ease with which the chemical link can be ruptured, and hence a measure of the strength of the bond. This procedure is often simpler to apply than direct thermal measurements.

The vibration-rotation spectra of diatomic molecules are the simplest to interpret, for the molecule can vibrate only in one way, namely in and out along the line joining the nuclei, but more complex molecules have more modes of vibration and rotation and the results are often very difficult to interpret. Many useful results have been obtained;

thus it is found that the carbon dioxide molecule has only one mode of rotation. This is in keeping with a linear structure $O=C=O$, for if the molecule were triangular, there would be three different moments of inertia.

Raman spectra are also useful in connection with constitutional problems. Such spectra are obtained by throwing a beam of mono-chromatic light on to the substance under examination, and the wave-length of the scattered light is measured at right angles to the direction of the incident light. Most of the scattered light is of the same frequency as the incident, a small proportion is of greater wave-length, and a few molecules give up energy to the incident light and faint lines of greater frequency than the incident light are observed. The change in frequency (Raman effect[1]) takes place within the visible range of the spectrum and is due to the vibrations of atoms with definite linkages. It is therefore characteristic of each type of grouping in the molecule and the change in wave-length is independent of the wave-length of the incident light. Determinations of such frequency shifts therefore, are valuable; for example the shifts observed for phosphorous acid[2] support the formula $O \, PH(OH)_2$ for this substance.

Colour of Ions.—The atomic numbers of those elements which give coloured ions lie in close proximity to one another. The ions of elements of atomic number 1-21 (H to Sc) are colourless. In the elements which follow, having the atomic numbers 22-29 (Ti, V, Cr, Mn, Fe, Co, Ni, Cu), the ions are coloured, at any rate in certain states of valency. Then follow (atomic Nos. 30-40, Zn-Zr) colourless ions, then (41-46, Nb-Pd) coloured, followed by (47-56, Ag-Ba)[3] colour-less, etc., etc. Generally, those elements giving rise to coloured ions and compounds are the transition elements of Bohr's classification (p. 25).

The colour of the ions is due to the oscillations of the outer electrons. According to a conjecture originally made by R. Ladenburg,[4] the arrange-ment of the outer electrons in a single layer meets with resistance in these cases and there is present an intermediate level and an outer level. The result of this subdivision is a mobility of the electrons which does not obtain in the inert gases and which is in agreement with the formation of compounds of varying valency by these elements. The ions of these elements are actually colourless when there are eighteen electrons in the layer next the outermost, e.g. in the cuprous compounds in the first group, in the quadrivalent titanic compounds in the fourth group, and in the quinquevalent vanadium compounds in the fifth group. The electron orbits in the double layers are easily disturbed.

[1] Raman, *Indian J. Physics*, 1928, 2, 399; *Trans. Faraday Soc.*, 1929, 25, 781.
[2] Ananthaknishnan, *Nature*, 1936, 138, 803.
[3] Coloured bivalent Ag compounds are now known (p. 699).
[4] *Z. Elektrochem.*, 1920, 26, 269.

Magnetic Properties.—Substances like iron, which tend to set themselves along the lines of force in a magnetic field, are called ferro-magnetic. This power is possessed by many other substances though usually to a markedly less extent; they are called para-magnetic, while substances which take up a position at right angles to the lines of magnetic force are known as dia-magnetic, but this property is never highly developed. The ferro-magnetic elements are iron, cobalt and nickel. Ferro-magnetism is only slightly influenced by variation of temperature, at low temperatures; it shows a slight decrease when the temperature is raised. At certain temperatures (for iron 760°, cobalt 1100°, nickel 350°) it disappears almost completely, and its reappearance when the temperature is lowered is equally sudden and complete (*cf.* p. 864). Under the influence of temperature, the magnetic suscepti-bility of the elements which are not ferro-magnetic undergoes variation ; several remain almost unaffected up to 1100° (diamond, crystalline boron, Mo, W, Os), while the susceptibility of others varies in a regular manner with increase or decrease of temperature, and even at the melting point their behaviour shows no sudden irregularity (K, Mg, Zn, In, S, Se). With others (Ag, Au, Tl, Pb, Bi, Sb, Sn, Te, P) the susceptibility changes irregularly on fusion. The susceptibility curves of elements of yet another group do not show a jump at the melting point, but only a slight break (Na, Cd, Al, I). The points at which other changes occur are often recognisable by the discontinuity of susceptibility (Tl, Zn), but this is not always the case (Sn, Ti). Para-magnetism is due to the presence in the atom, ion or molecule of an incomplete electron group involving an unpaired spin (see p. 4). If the electron groups are all complete, all spins are paired, the electrons compensate each other, and the substance is diamagnetic. The quantum theory of paramagnetism[1] has dealt successfully with many of the experimental results. It relates the behaviour of the electrons, which constitute the elementary magnets, to the spectroscopic state of the ions. The electrons possess angular momentum because of their orbital motion about the nucleus and also because of their spin motion ; in crystals the first is limited, but the second is unaffected. As examples of the application of magnetic measurements to valency problems, ions of transition group elements are paramagnetic, *e.g.* the double sulphates, $M^{II}SO_4 . (NH_4)_2SO_4 . 6H_2O$, where M^{II} is Fe, Co, Ni, Mn ; but $ZnSO_4 . (NH_4)_2SO_4 . 6H_2O$ is diamagnetic. Rare earth salts with incomplete shells and uncoupled spins are also paramagnetic, dysprosium compounds being amongst the most strongly paramagnetic substances. Univalent silver and copper compounds have zero moment, but bivalent silver and copper are paramagnetic in keeping with the presence of one unbalanced electron.[2] In the univalent condition these ions have a

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[1] See Schlapp and Penney, *Reports on Progress of Physics*, 1935, 2, 60.
[2] Sugden, *J. Chem. Soc.*, 1932, 161.

complete sub-group of 10 electrons (in 3_8 level for Cu and 4_8 level for Ag) and hence are diamagnetic. In the bivalent ions, they have 9 electrons in this sub-group ($s=\frac{1}{2}$ and $l=0$, 1 or 2, see p. 4) and hence are paramagnetic. "Odd molecules," *e.g.* NO, ClO_2, NO_2 (see p. 56) also are paramagnetic.

Valency of the Elements

Nature and Formulation of Valency.—Valency may be considered (see p. 11) under the following five types: (1) electrovalency, (2) covalency, (3) co-ordinate valency, (4) odd electron valency, (5) field valency. It must be realised, however, that except in limiting cases, chemical bonds exhibit the properties of more than one type of valency; for example, covalent bonds often appear to be partially ionic (electrovalent), while many predominantly electrovalent bonds exhibit some covalent character. Many valency problems still await solution. Co-ordination and field valency will be discussed when the co-ordination compounds are considered (p. 279).

The valency relations are clearest in electrovalent (polar) compounds. In these a complete outer layer of electrons is achieved by a transference of electrons, either by adding on more electrons or by losing those already present in the outside layer. For example, an element with five electrons in the outer layer might give up these valency electrons and become a quinquevalent positive ion, a "stripping" taking place to expose the complete inner shell, initially one place removed from the outermost shell; or by taking up three electrons to complete the outermost layer, become a tervalent negative ion. Similarly, an element with four electrons can become either a positive or negative quadrivalent ion by surrender or accretion of four electrons. The sum of the positive and negative electrovalencies is therefore normally equal to eight as first pointed out by Abegg,[1] who described the positive effect as valency and the negative as contravalency. In the first series of the periodic system the positive and negative valencies are as follows:—

Group.	I.	II.	III.	IV.	V.	VI.	VII.	0
	Li	Be	B	C	N	O	F	Ne
+ Valency	1	2	3	4	5	6	7	8
− Valency	7	6	5	4	3	2	1	—

The higher positive valencies are not often observed, for the surrender of so many electrons is resisted by the electrostatic forces present in the atom. Similarly, the higher negative valencies do not often appear owing to the repulsion of the electrons already present in the atom, but there are some well-defined co-ordination compounds

[1] *Z. anorg. Chem.*, 1904, 39, 342.

in which the shell of the next inert gas is attained. Elements with few electrons in the outer layer, for instance, alkali and alkaline earth metals, practically never form negative ions.

Many elements have several valencies. Among the metals the outer electrons are frequently not all given up in the lower valencies, particularly with metals of high atomic number. As has been suggested on p. 47, the outer electrons in these elements are possibly divided into two sub-layers, and the electrons which are not given up are in an intermediate layer. The variable valency of such metals as copper, chromium, manganese and the iron group can be explained on this basis. In other cases the element has a different valency, merely because in one compound it gives up electrons, while in another it takes them up. The variations of valency are, however, more often due to the fact that some of the compounds are electro-valency compounds and some covalency compounds, particularly among the non-metals. NaCl, for instance, is a typical electrovalency compound, while Na_2O_2 is covalent. The variable valency of such non-metals as sulphur or nitrogen is usually due to the formation of covalent compounds (cf. pp. 575, 676). Electrovalent or polar compounds in general are less volatile than covalent compounds.

In order to understand the valency relations in covalent compounds, the ideas implied in Lewis's Octet theory (p. 13) must be realised. The number of electrons which can be shared is limited by the principle that the octets of the atoms or ions which thus attach themselves must remain undisturbed. It may be noted that the electrons are almost always shared in pairs.

$$H—O—H \qquad O{=}C{=}O \qquad H—C{\equiv}C—H \qquad H—I$$

$$H_{\times}^{\cdot}O^{\times}H \qquad \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{\overset{\times}{\underset{\times}{C}}}{\overset{\times}{\underset{\cdot\cdot}{C}}}\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} \qquad H^{\times}C{::}C_{\times}H \qquad H_{\times}^{\cdot}\overset{\cdot\cdot}{\underset{\cdot\cdot}{I}}{:}$$
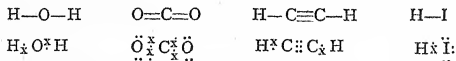
The electrons are indicated by · and x according to the atom to which they originally belonged—there is naturally no difference between them.

In such compounds, each element by the process of sharing reaches the electronic shell of the next succeeding inert gas; thus hydrogen attains the helium shell, carbon the neon shell, iodine the xenon shell, and so on. Stable compounds may sometimes be formed even if the outermost shell contains less than eight electrons, e.g. in boron tri-chloride, BCl_3, boron has a shell of six electrons. In other compounds the shell may exceed an octet; sulphur hexafluoride SF_6 probably falls in this class, the sulphur having a shell of twelve electrons. In these formulations, two electrons constitute each covalency, but in order not to exceed the octet, some writers postulate single electron linkages (see below) in such compounds.

As has already been mentioned, there are intermediate stages

between the true covalency and electrovalency, and the measurement of dielectric constants of such substances, leading to the calculation of their dipole moments[1] are of considerable significance. In many covalent compounds one of the two electrons is contributed by each of the linked atoms if the bonds are single; in double bonds, four electrons constitute the linkage, two being supplied by each atom; water, carbon dioxide, and acetylene, shown above, are examples. A notation, introduced by Main Smith, is useful in dealing with these and other compounds; each shared electron is shown by a line thus ——, and the number of unshared electrons in the outermost shell is indicated by a numeral placed against the symbol of the element. Thus water, carbon dioxide and acetylene are written:

$$H=O^4=H \quad , \quad O^4\equiv C\equiv O^4 \quad , \quad H=C\equiv\equiv C=H.$$

To determine the electric charge centred on each element in the compound, each shared electron is counted as $-\frac{1}{2}$, each unshared electron as -1, and this total is summed with the core charge of the atom, *i.e.* the charge present on the atom stripped of its shell of valency electrons; thus the core charge of hydrogen is $+1$, of carbon $+4$, of oxygen $+6$, etc. In the above compounds the resultant charges are all zero. Electrical neutrality is similarly met with in many other compounds, but in some, charges are centred on certain elements; phosphorus trichloride and oxychloride are good examples:

$$
\begin{array}{ccc}
& Cl^6 & \\
& \| & \\
Cl^6\!=\!\!P^2 & \text{and} & \\
& \| & \\
& Cl^6 &
\end{array}
\qquad
\begin{array}{c}
Cl^6 \\
\| \\
Cl^6\!=\!\!\overset{+}{P}\!=\!\overset{-}{O}{}^6. \\
\| \\
Cl^6
\end{array}
$$
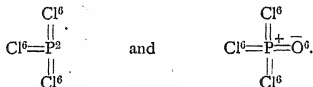
Summation of charges gives $+7-6-1=$ zero for chlorine in both compounds, and $+5-3-2=$ zero for phosphorus in the trichloride. In the oxychloride, however, the charge on phosphorus is $+5-4=+1$, and on oxygen is $+6-6-1=-1$. This is indicated by a positive sign written against the symbol for phosphorus, and a negative sign against oxygen. Adopting other notations, this compound is written

$$
\begin{array}{c}
Cl \\
| \\
Cl-P=\!=O \\
| \\
Cl
\end{array}
$$
by Sudgen, who called this type of linkage a semi-polar

$$
\begin{array}{c}
Cl \\
| \\
Cl-P\!\rightarrow\!O \\
| \\
Cl
\end{array}
$$
double bond, and by Sidgwick, who refers to it as a

---
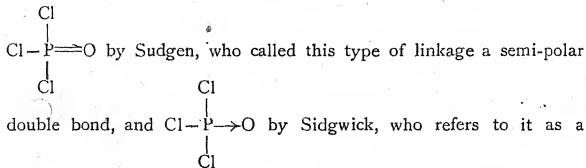
[1] See for example, *Dipole Moments*, Le Févre, London, 1938; *Recent Advances in Physical Chemistry*, chapter iii, Glasstone, London, 1936.

co-ordinate link, and considers that this type of bonding is frequently found in co-ordination compounds. In pre-electronic formulae these bonds were shown as double bonds, e.g. $Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{P}}=O$, with nothing to distinguish them from the non-polar double bonds, present, for example, in carbon dioxide or ethylene. It is now recognised that the "double bond" present in phosphorus oxychloride consists of only two electrons, both of which are supplied by the same atom. The atom contributing the two electrons is sometimes referred to as the donor, and that receiving the electrons as the acceptor. The donor atom, prior to the combination, must have an unshared pair or "lone" pair of electrons. The bond is in a sense an electrovalency superimposed on a covalency, and in that sense the bond is double ("semi-polar double"). The direction of the arrow heads in Sugden's and Sidgwick's notations show the direction of the electron transference. Amongst compounds which contain this type of linkage, the following may be taken as examples :

$$H{=}O^4{=}\overset{+}{\underset{}{Cl}}{}^2{=}\bar{O}^6 \qquad H{=}O^4{=}\overset{++}{\underset{}{Cl}}{}^2\overset{\nearrow O^6}{\underset{\searrow \bar{O}^6}{}} \qquad H{=}O^4{=}\overset{+++}{\underset{}{Cl}}\overset{\nearrow\!\!\nearrow \overset{..}{O}{}^{ii}}{\underset{\searrow O^6}{}}$$

$$\overset{H{=}O^4}{\underset{H{=}O^{4'}}{}}\overset{+}{\underset{}{S}}{}^2{=}\bar{O}^6 \qquad \overset{H{=}O^4}{\underset{H{=}O^{4'}}{}}\overset{++}{\underset{}{S}}\overset{\bar{O}^6}{\underset{\bar{O}^6}{}} \qquad \overset{Cl^6}{\underset{Cl^{6'}}{}}\overset{+}{\underset{}{S}}{}^3{=}\bar{O}^6$$
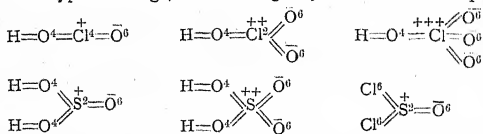
They can of course be formulated by the other methods, for example :

$$\overset{H-O}{\underset{H-O}{}}{>}S\overset{\nearrow O}{\underset{\searrow O}{}} \qquad , \qquad \overset{H-O}{\underset{H-O}{}}{>}S\overset{\diagup\!\!\diagup O}{\underset{\diagdown\!\!\diagdown O}{}}, \text{ etc.}$$
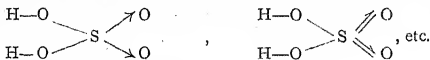
These and other compounds containing this type of linkage will be dealt with in the course of the book.

Some of the earliest experimental evidence for semi-polar bonds was afforded by measurements of parachors. As has been mentioned on p. 39, the parachor of a compound can be calculated by adding together separate parachors of the atoms contained in it, and the structural parachors of the valencies which are operative. When the parachors can be determined experimentally and the atomic parachors are known, this obviously gives a means of distinguishing between the different kinds of linkages. The structural parachors found are :

Single covalency or non-polar bond	.	.	.	o	units
Double	,,	,	,,	,,	.	.	$+23\cdot2$,,
Triple	,,	-	,,	,,	,,	.	.	$+46\cdot4$,,
Semi-polar double bond	.	.	.	.	.	$-1\cdot6$,,

Thus in compounds containing semi-polar double bonds, a subtraction

of 1·6 units has to be made, instead of an addition of 23·2 units required in the case of compounds containing non-polar double bonds. Other measurements, based, for example, on volatility or dipole moments also show the presence of this type of bonding.

In some compounds, such as PCl_5, it is necessary to assume that phosphorus either has a shell of ten valency electrons if each chemical bond consists of two electrons, or if the valency shell of phosphorus is an octet, then two of the bonds must consist of single electrons, *i.e.*

$$Cl^6 \underset{Cl^6}{\overset{Cl^6}{\underset{P}{\parallel}}} Cl^6 \qquad \text{and} \qquad Cl^6 \underset{Cl^6}{\overset{Cl^6}{\underset{P}{\parallel}}} \underset{\overset{-\frac{1}{2}}{Cl^7}}{\overset{-\frac{1}{2}}{Cl^7}}$$
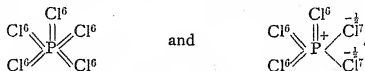
Sugden considers that parachor evidence favours the second formula. The one electron linkage, or singlet linkage, or semi-polar single bond requires a subtraction of 12·4 units, and the observed parachors of many substances agree with the values calculated in this way. There is, however, much evidence in favour of the ten electron shell for phosphorus and the duplet linkage. A general argument, based on the stability of such compounds as PCl_5, SF_6, OsF_8 is often used in support of the duplet as opposed to the singlet formulation, and computations of bond distances, based on electron diffraction, also support the duplet link. Quantum mechanical considerations also indicate that in favourable circumstances larger electron shells than the octet may be produced. In some compounds, for example the boron hydrides, singlet linkages may be present.

Often it is not possible to decide in favour of any one of such formulae, and no doubt the molecules consist of *a single variety* intermediate between such forms ; although they are only of one form, they cannot be represented by a single formula in our existing notation, and they must not be regarded as tautomerides, but as *resonance hybrids*.

Considerable modifications of the above theories have developed from the application of the concept of resonance to the problem of the nature of the chemical bond. In the quantum mechanical treatment of a system such as the molecule, consisting of positively charged nuclei and negative electrons, complete description of the system is possible only if the conjugated momenta of the particles as well as the ordinary dimensions of space are taken into consideration. The resulting description takes the form of a wave function, which is different for each structure, and from which the energy corresponding to a given structure may be calculated. If the molecule is in its normal (most stable) state, the correct wave function gives a lower energy than does any other reasonable wave function ; *i.e.* the structure whose wave function gives the lowest energy is the most stable structure.

The simplest possible structure to which this treatment has been applied is the hydrogen molecule-ion, H_2^+ the existence of which was recognised from the spectrum of hydrogen. We may regard this system as the result of the approach of a hydrogen atom and a hydrogen ion, and if we designate these $H_A^.$ and H_B^+ it is clear that the system may equally well be represented by $H_A^.$ H_B^+ and H_A^+ $\cdot H_B^.$. The energy of the system, calculated in terms of internuclear distance from the wave functions of the two parts, shows no minimum value at any finite internuclear distance. If, however, a composite wave function is employed, taking into account resonance between the two structures given above, a pronounced minimum occurs at an internuclear distance of about 1·06 Å. A contour map of the electron distribution of the system indicates that the electron spends by far the greatest part of its time between the two nuclei, scarcely ever getting on the far side of either. In the hydrogen molecule-ion, therefore, there may be formed a one-electron bond which is stabilised by the resonance of the molecule between the two equivalent structures Such a bond, which is only possible between atoms which are very nearly, or quite, alike in electronegativity, has a little more than half as much energy as the electron-pair bond (*vide infra*).

The hydrogen molecule provides us with a simple example of the covalent electron-pair bond. Here we have two electrons which may, in the extreme, take up the positions indicated by $H_A^{.1}$ $^{2.}H_B$, $H_A^{.2}$ $^{1.}H_B$.

The Heitler-London wave-mechanical treatment of the hydrogen molecule indicates the formation of a stable electron-pair bond when the internuclear distance is 0·79 Å, while a more refined calculation gives the distance as 0·75 Å, within 0·01 units of the observed value. This treatment takes into account resonance between the two structures given above, and it is significant that the bond energy calculated on this basis is about 80 per cent. of the observed value. The energy of the electron-pair bond, therefore, is mainly that of the resonance of the two electrons between the two atomic orbitals. It is important to note that in the formation of a stable electron-pair bond, the spins of the electrons must be opposed, *i.e.* the electrons must be "paired." Besides the covalent structure represented by H — H, the ionic structures H_A^+ H_B^- and H_A^- H_B^+ (*i.e.* H+ :H− and H:− H+) contribute to the normal state, but only to a very small extent, viz., about 2 per cent.

Similar methods may be used in dealing with bonds between unlike nuclei, but since there will be, in general, a difference in electronegativity between the nuclei, ionic (electrovalent) structures may also contribute to the normal state of a molecule, as well as the covalent structure. For instance, the water molecule may be represented

as a resonance hybrid of the following forms, each contributing to the bond energy of the normal state in the proportions shown :

$$
\begin{array}{cccc}
\text{H} & \text{H} & \text{H}^+ & \text{H}_+ \\
:\ddot{\text{O}}:\text{H} & :\ddot{\text{O}}:^-\text{H}^+ & :\ddot{\text{O}}:^-\text{H} & :\ddot{\text{O}}:\overset{=}{\text{H}}_+ \\
0.37 & 0.24 & 0.24 & 0.15
\end{array}
$$

while a number of structures go to make up the normal state of the ammonium ion :

$$
\begin{array}{ccc}
& \text{H}^+ & \text{H}^+ \\
\text{one H} :\overset{+}{\ddot{\text{N}}}: \text{H}, & \text{four H} :\ddot{\text{N}}: \text{H}, & \text{six H} :\overset{-}{\ddot{\text{N}}}:^- \text{H}^+, \\
\text{H} & \text{H} & \text{H}
\end{array}
$$

$$
\begin{array}{cc}
\text{H}^+ & \text{H}^+ \\
\text{four H} :\ddot{\text{N}}:^= \text{H}^+, & \text{and one H}^+ :\ddot{\text{N}}:^= \text{H}^+. \\
\text{H}^+ & \text{H}^+
\end{array}
$$
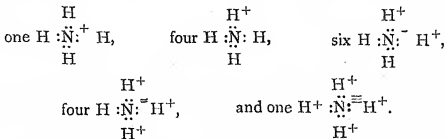
The covalent bond is thus seen, as a general rule, to exhibit partial ionic character. A further factor which must be taken into account is the deformation of one atom forming a covalent bond by the other forming the same bond. In the case of the H_2 molecule, deformation accounts for about 15 per cent. of the bond energy. A quantitative treatment of the whole problem is beyond the scope of this book, but it may be pointed out that measurements of dipole moments, interatomic distances and thermal relations have led Pauling to establish an electronegativity scale of the elements, with the aid of which it is possible to make an approximate estimate of the extent to which covalent character, electrovalent character and resonance contribute to bond energies in a large number of compounds.

Directed Covalent Bond.—The resonance energy of a bond depends on the amount of overlapping of the atomic orbitals; the greater this overlapping (*i.e.* the greater the region in which large values of the orbital wave functions coincide), the greater the energy of resonance. Consequently the strongest bonds will be formed in the direction in which there is greatest overlapping. This principle, together with the fact that stable bonds are formed only by stable atomic orbitals, forms the basis of modern ideas on the direction of covalent bonds. As the electron distribution in the *s*-orbital is spherically symmetrical, this orbital would be expected to show no preference to form bonds in one direction rather than in any other. The electron distribution in the three *p*-orbitals shows them to be directed at right angles to each other. Clearly, therefore, overlapping with atomic orbitals of other atoms is greatest in these three directions, so that covalent bonds involving *p*-orbitals would be expected in directions mutually at right angles. This is found approximately to be the case; *e.g.*

$$
\text{O} \begin{array}{c} \diagup \text{H} \\ \diagdown \text{H} \end{array} 104° \ 31' \quad , \quad \text{O} \begin{array}{c} \diagup \text{F} \\ \diagdown \text{F} \end{array} 200°, \text{ etc.}
$$
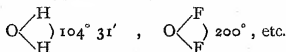
The divergence is explained to some extent by the partial ionic character of the covalent bonds, which leads to some degree of repulsion between, for instance, the hydrogen atoms of water. Considerations of the angular electron distribution also indicate that the strengths of p-p, p-s, and s-s bonds decreases in the proportion $3 : \sqrt{3} : 1$.

The element carbon provides an interesting example of the application of the modern theory of valency. The valency shell contains four electrons, one $2s$ and three $2p$. It might therefore be supposed that a carbon atom would form three strong bonds at right angles to each other by sharing its p-orbitals, while its s-orbital formed a third, weaker, bond in an arbitrary direction. If, however, it is assumed that the atom will tend to form bonds with the greatest possible energy (*i.e.* the atom having the least possible energy and being thus in its most stable condition), calculations show that a hybridisation of the four orbitals enables the formation of four equivalent bonds, each of which is stronger than either pure p- or pure s-orbital bonds. Further, these bonds may be shown to be directed towards the corners of a regular tetrahedron, thus affording a theoretical explanation of the well-established observation of the tetrahedral carbon atom.

This process of hybridisation may also occur in other cases, and particularly interesting results are obtained with the transition elements, which have a very marked tendency to form large, stable complexes. The $Co(NH_3)_6^{+++}$ ion, for example, may be considered. In this ion, the cobalt atom (at. no. 27) has four electron shells and twenty-four unshared electrons, which are distributed : $1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \ 3d^0$, leaving two $3d$-, one $4s$-, and three $4p$-orbitals available for bond formation. Mathematical treatment shows that these six orbitals are hybridised to yield six s-p-d orbitals, each capable of forming stronger bonds than any of the simple orbitals concerned. Moreover, these bonds are shown to be directed towards the corners of a regular octahedron ; this configuration had been established by experiment (see p. 296).

Similarly, in $Ni(CN)_4^=$, the orbitals available for bond formation (one $3d$, one $4s$ and three $4p$) are hybridised to give *four* bond-forming orbitals, directed towards the corners of a square. This square coplanar structure for nickelocyanides, which was predicted by Pauling, has been verified by experiment.

Just as in the hydrogen molecule-ion a one-electron bond is formed, so, it appears, a three-electron bond may occur in certain so-called " odd molecules," such as the helium molecule-ion, He_2^+, nitric oxide, nitrosyl chloride, the superoxide ion and the oxygen molecule. In He_2^+ we have resonance between the structures $He_A \cdot :He_B^+$ and $He_A^+ : He_B$, the formula being written $He \ldots He^+$. The bond is strong (bond energy = 55 k cal./mole.), having approximately the same bond energy as the one-electron bond in H_2^+.

Thus nitric oxide may be formulated $:N\!\!=\!\!O:$ and chlorine dioxide

$$:Cl \begin{matrix} \ddot{O}: \\ \\ :\ddot{O}: \end{matrix} \quad , \quad :Cl \begin{matrix} :\ddot{O}: \\ \\ \ddot{O}: \end{matrix}$$
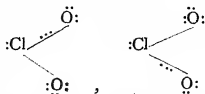
The proton itself can act as a bond between sufficiently electronegative atoms, particularly F, O, and to a lesser extent N and Cl. A discussion of the hydrogen bond will be found in the section on co-ordination compounds (p. 346).

Yet another characteristic type of bond is found in the metals. The rapid transmission of heat and electricity, and the general characteristics of ductility, malleability, etc., in metallic substances have led to the conception of a crystalline arrangement of spheres with free electrons in the interstices. The modern view is that there is a continuous set of energy levels for "free" electrons, the latter being so arranged that in the normal state they are paired, thus forming something approaching covalent bonds. In excited states, some of these pairs are disrupted, and the electrons thus lend themselves to magnetic orientation; *i.e.* the metal exhibits paramagnetism. Since the contribution of each unpaired electron to paramagnetic susceptibility decreases with increased temperature, however, the two effects cancel.

Further examples of the application of modern ideas of valency will be found in the descriptive sections of this book; for a comprehensive survey the reader is directed to Linus Pauling's monograph.[1]

Much new evidence is being brought to bear in various ways on valency problems. Sidgwick[2] says: "Our knowledge of structural chemistry has been greatly extended, especially in the last twenty years by many physical methods, based on absorption spectra in the infra-red, the visible and the ultra-violet and on Raman spectra, on the measurements of specific heats and heats of combustion, of the dielectric properties, and of the scattering of X-rays and electron waves, as well as on the study of chemical dynamics." These matters are now receiving a great deal of attention, and these new lines of approach will doubtless bring system to many of the facts dealt with in this book, which at present show little apparent connection.

General Rules of Valency.—The older empirical observations on valency and the formation of compounds are given below in so far as they are valuable.

---

[1] *The Nature of the Chemical Bond*, L. Pauling , Cornell University Press, 1940.
[2] *J. Chem. Soc.*, 1936, 533 ; see also Sidgwick and Bowen, *Ann. Rep. Chem. Soc.*, 1931, 28, 367-403.

The Hydrogen Valency.—The following scheme shows the number of hydrogen atoms with which elements in the various groups combine [1]:

Group .	.	.	0	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Hydrogen atoms	.	.	0	1	2	3	4	3	2	1	0

There is a regular increase in valency up to the fourth group, followed by an equally regular decrease, due to the hydrogen functioning as a negative element towards the elements of the earlier groups, while it behaves as a positive element to those of the later groups. Hydrogen removes an electron from the lithium atom, for instance, so that when molten LiH is electrolysed the hydrogen appears at the anode.[2] On the other hand, an electron is given up to the fluorine atom by the hydrogen atom so that on electrolysis of hydrofluoric acid the hydrogen is found at the cathode. No other element can behave in this way and so no other element gives this increase and decrease in valency in traversing a series. The valency of hydrogen is also unity in covalency compounds, as it has only one electron to share with other atoms.

The valency of hydrogen remains the same in all its compounds; it is therefore possible to ascertain the formulae of these compounds, if the valency of the other element is known, provided that only one atom of this element is contained in the compound. If, on the other hand, several atoms of the other element are present, the formula of the hydrogen compound cannot be definitely predicted (N_2H_4, N_3H_6; C_2H_6, C_2H_4, C_2H_2; B_2H_6; also in the hydrides of silicon and phosphorus); in certain cases one atom of hydrogen can unite two other atoms (see co-ordinated hydrogen, p. 346).

The Oxygen Valency.—The maximum valency of the elements in respect to oxygen is usually the same as the number of the group to which they belong; there exist, however, so many exceptions to this rule that it can only be used as a general statement.

While oxides often exist whose formulae can be ascertained if the elements are credited with a valency representing the number of their group in the periodic system, these oxides do not always represent the maximum or minimum valency, but may be intermediate, as in nitrogen and sulphur.

In the lower series of the periodic system the oxides of those elements which lie close to the fourth group support the hypothesis that their maximum valencies represent the group numbers of the elements; oxides of elements in the groups at the ends of the table usually deviate from this rule. In the middle groups a number of oxides occur with lower oxygen content than is required by their

[1] With the exception of certain hydrides discussed in Chap. XXIX, which cannot be dealt with satisfactorily by ordinary valency rules.

[2] Moers, *Z. anorg. Chem.*, 1920, 113, 179.

positions in the system (PbO, SnO, Sb_2O_3, as well as PbO_2, SnO_2, Sb_2O_5). In the eighth group the oxygen valency is the most irregular:

Highest Oxides of the Eighth Group

Fe_2O_3	Ni_2O_3	Co_2O_3
RuO_4	RhO_3	PdO_2
OsO_4	IrO_2	PtO_3
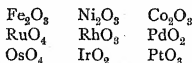
The anticipated octavalency is attained only in osmium and ruthenium; the maximum valencies of the other elements towards oxygen are usually much lower. In other groups the required degree of saturation is surpassed (CuO, where only Cu_2O might be expected). This is especially so in Group I, where the combining capacity might be expected to be very low.

The Halogen Valency.—In the first four groups of the periodic system the maximum valency towards a halogen is always the same as the number of the group, the only exceptions being in the halogen compounds of copper and gold, in which the valencies of the higher oxides of these metals (*i.e.* bivalency and tervalency) occur. The iodide of copper is obtained only in the univalent form.[1] But with

Maximum Halogen Valencies of the Elements of Groups IV—VIII.

IV.	V.		VI.		VII.	VIII.		
Fluoride	$N\,3/3/3$		$O\,2/2/\tfrac{2}{3}$		$F\,I$			
Chloride								
Bromide								
Iodide	$P\,5/5/5/3$		$S\,^4_1 6/O$		$Cl\,^I_I 3/I/II$	$Fe\,^3_3 3/\tfrac{8}{3}$	$Co\,^2_2 3/2$	$Ni\,^2_2 3/2$
	$V\,^4_3 ?/3$	$As\,^3_3 5/3$	$Cr\,^3_3 3/3$	$Se\,^4_4 6/O$	$Mn\,^2_2 3/2$	$Ru\,^4_3 ?/3$	$Rh\,^3_3 3/?$	$Pd\,^2_2 3/2$
	$Nb\,^5_5 5/?$	$Sb\,^5_3 5/3$	$Mo\,^6_6 3/4/4$	$Te\,^4_4 6/4$	$Br\,^I_I 5/I/7/I3/I$			
	$Ta\,^5_5 ?/5$	$Bi\,^3_3 5/3$	$W\,^6_6 6/4$		$Re\,5\ 6$	$Os\,^8_6 8/4$	$Ir\,^4_4 6/4$	$Pt\,^4_4 4/4$
$Pb\,^4_2 4/2$			$U\,^6_5 6/4$					

[1] A bivalent iodide of copper can occur in more complex compounds. (For example $[Cu(NH_3)_6]I_2$.) Silver also forms bivalent complex compounds (p. 699).

the last member of Group IV, lead, commence the irregularities which occur over a large portion of the right-hand side of the system.

In the table (p. 59) the figures placed beside each element, when read downwards, represent the maximum valency of these elements to fluorine, chlorine, bromine and iodine.

It is observed that the number of atoms of halogen combining with one atom of the other elements decreases with increase in the atomic weight of the halogen. Although in Groups V and VI the fluorides frequently show the normal quinque- and sexa-valency, the chlorides often fall short of this; moreover, from the bromides to the iodides, the decrease in valency is so marked that only one element (tantalum) displays the quinquevalency towards iodine which is to be expected from its position in the system.

In Groups VII and VIII the valency is quite irregular, IF_7 and $OsCl_8$ being the only compounds showing septa- or octa-valency towards the halogens; the greatest variations occur among the non-metals (the top right-hand side of the table).

In general, the maximum valency of elements occurring in the first four groups of the periodic system towards more highly negative elements is identical with their group number in the system (the only exceptions are in Cu, Au, and partly in Pb), provided electrovalent compounds only are considered.

Valency and Chemical Character.—There is a great similarity between the elements occurring in the same vertical group of the periodic system; but between the elements in the two sub-groups of the same group the resemblance is not so strong, and it gradually decreases the further the groups are from the centre of the system— it is least in the elements of Groups I and VII.

```
           Li                              F
           Na                              Cl
          /                               /
        K    Cu                        Mn    Br
       /      \                       /        \
     Rb        Ag                   Ma           I
    /            \                 /
  Cs              Au             Re
```
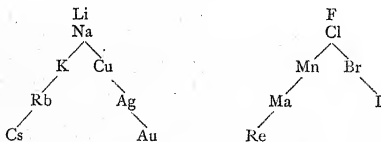
Similarity in chemical properties is to a great extent dependent on similarity in valency. A comparison of different stages in valency, even in elements which belong to the same group, is of little value. Conversely, a very marked likeness is found to exist among elements belonging to different groups of the system when they exhibit the same valency, particularly when they have about the same atomic volume; for example, tervalent aluminium, chromium and iron (Groups III, VI and VIII) give compounds of an identical crystalline form, very similar in solubility, reactive power, etc.

Elements of different valencies sometimes form compounds which closely resemble one another—this is shown by the pairs of elements Li-Mg, Be-Al, B-Si; it is often seen in elements which, instead of being adjacent to or beneath each other in the system, are placed diagonally under each other (from left to right). This similarity is highly important, and is so pronounced in compounds of beryllium and aluminium that for a long time the bivalency of beryllium was doubted. Similar relationships are also found lower in the system: vanadium and molybdenum, niobium, tantalum and the rare earths can all form compounds which closely resemble one another, in spite of differences in the standard valency of these elements.

Compounds of the Inert Gases.—Electro- or co-valent compounds cannot be formed by the inert gases, as their electron shells are complete and there is no tendency either to lose or gain electrons. The inertness of these elements is not so great as has often been supposed. Several of them form hydrates containing $6H_2O$, analogous to the other hydrates of elementary gases. They are formed by introducing water vapour into an atmosphere of the gas at low temperature. The solid crystalline bodies thus formed are of varied stability, the decomposition temperatures under atmospheric pressure being: argon hydrate, $-24.8°$, krypton hydrate, $-39.2°$, xenon hydrate, $0°$. The latter is stable at $+23.5°$ under 23.5 atmospheres pressure. These compounds are probably field valency compounds, the nature of which will be discussed later. Booth and Willson[1] made a phase-rule study of the system boron trifluoride argon, and detected compounds A, nBF_3 where $n=1, 2, 3, 6, 8$ and 16; the compounds are unstable and dissociate above their melting points. These authors consider that combination takes place by the completion of the boron octet and formation of co-ordinate linkages (see p. 52), $F_3B \longleftarrow A$; on this view, however, compounds in which n exceeds 4 should not be obtained. Like the hydrates, these compounds are probably of the field valency type. A compound of xenon with phenol, $Xe2C_6H_5OH$, has been prepared.[2]

Helides, compounds of helium with other elements, can be made in various ways, and may be either electro- or co-valency compounds. Among these are the compounds with mercury, iodine, sulphur and phosphorus formed under the influence of glow discharges or electron bombardment. A tungsten helide, WHe_2, made by electrical disintegration of tungsten in a helium atmosphere, has been studied in some detail.[3] The gaseous mercury helides[4] $HgHe$ and $HgHe_{10}$ have recently been questioned; a gaseous bismuth helide appears to be

[1] *J. Amer. Chem. Soc.*, 1935, **57**, 2273.
[2] Nikitin, *Compt. rend. Acad. Sci. U.R.S.S.*, 1940, 29, 251.
[3] Boomer, *Nature*, 1925, 115, 16; *Proc. Roy. Soc.*, 1925, 109, 198.
[4] Manley, *Nature*, 1924, 114, 861; 1925, 115, 337, 948.

confirmed,[1] but it occurs in such small quantities that it can be detected only by refined methods such as are used in radioactivity work. Hydrogen compounds HeH^+ and HeH_2^+ can be detected by the mass spectrograph, but their life period is only of the order of 10^{-8} seconds. The diatomic helium molecule He_2 can be compared with the helides; its existence is shown by the band spectrum of helium.

Under the influence of strong stimuli the atoms of the inert gases can lose electrons and thus be brought into an ionised condition. The α-rays of radioactive substances, moreover, consist of helium atoms which have lost both their electrons and are thus naked nuclei with a double positive charge (cf. p. 65). But even in the forms of helium in which no electrons have been lost, the two electrons need not be part of the same shell, though the behaviour of these structures as regards valency cannot be determined. The ordinary form of helium, in which the two electrons move in intersecting one-quantum orbits (para-helium) can be transformed into ortho-helium, as shown by observations on its spectrum ; in this form one electron is in a 1_1 orbit and the other is in a 2_1 orbit. This form must be analogous to an alkali metal or to hydrogen, as it contains one outer electron, and must be reactive.

[1] Morrison, *Nature*, 1927, 120, 224.

RADIOACTIVE ELEMENTS AND ISOTOPES

Isolation—The rays—Disintegration products—Decomposition of atoms—Isotopes —Some radioactive products—Nuclear disintegration—Artificial radioactivity

COMPOUNDS of uranium and thorium blacken a photographic plate, even when the latter is wrapped in black paper; they discharge a charged electroscope placed near them, and cause a surface coated with hexagonal zinc sulphide (Sidot's blende) or barium platinocyanide $Ba[Pt(CN)_4]$, to glow. They are thus themselves sources of energy, but produce this energy over such a long period of time that the accompanying changes can be detected only by the most delicate means. They show their activity by the rays they emit. These phenomena were discovered in uranium compounds by Becquerel,[1] in thorium compounds by Schmidt[2] and Mme. Curie,[3] who first called them radioactivity; the most characteristic member of the group, first isolated by her from uranium compounds, was called radium.

Methods of Extraction.—Substances with very marked radioactive properties can be separated from the natural uranium and thorium compounds by ordinary chemical and physical operations. These substances differ from one another, but are to some extent inter-related. Most of the ordinary analytical methods are applicable to their separation. For example, if a solution of a uranium compound is treated with ammonium carbonate a precipitate is obtained which redissolves in excess of the reagent to form ammonium uranyl carbonate; but an insoluble residue (UX) remains behind, which resembles thorium rather than uranium in its chemical properties; for example, it can be precipitated from acid solutions by ammonia. This precipitate contains the whole of the penetrating radiation originally found in the uranium preparation, and so must be the source of it. In a similar manner a constituent which resembles barium rather than thorium in its chemical properties can be obtained from thorium salts. The radioelements thus show chemical properties which differ from those of the parent substance with which they occur. Their chemical behaviour assigns them to a place in the final series of the Periodic Table, where they occupy some of the gaps which previously remained empty.

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[1] *Compt. rend.*, 1896, **122**, 420.   [2] *Wied Ann.*, 1898, 64, 720.
[3] *Compt. rend.*, 1898, **126**, 1101.

The chemical differences between the radioelements are paralleled by different electro-chemical properties, so that they can be separated by electro-chemical methods, such as the electrolysis of a solution with graded voltage. The lowest voltage gives the most noble metal present, and the baser metals can be deposited on the anode as oxides. Thus polonium can be brought down on the cathode as metal or on the anode as peroxide. Markwald[1] used an elegant method of separating polonium by placing a stick of pure bismuth in a solution containing the mixture of bismuth and polonium; as the latter is the more electro-negative of the two metals its ions are discharged by the bismuth and it is deposited as a coherent coating on the bismuth rod, while the bismuth goes into solution. A similar method serves to separate RaC from RaB, for the former and not the latter is deposited from a solution by metallic copper.

Sometimes these substances can be separated by purely physical methods. Thus polonium can be parted from bismuth by taking advantage of its greater volatility, and UX from uranium as the solubilities of their salts are different; on fractional crystallisation the UX salt remains in the mother liquor. The uranium salts, on the other hand, are more soluble in organic solvents (ether, acetone) than those of UX.

Adsorption methods are very important as a means of separating the radioelements. Their salts are adsorbed by substances such as charcoal, metallic hydroxides, etc., but they are particularly easily adsorbed by substances which resemble them chemically. In this effect something more than mere adsorption takes place, possibly with penetration into the crystal lattice of the adsorbent, so that a kind of isomorphous mixture or mixed crystal is formed. Thus UX_2, which resembles tantalum, but is not an isotope of it, can be separated from UX_1, which resembles thorium. If a solution containing both of them is treated with solid tantalic acid, only the UX_2 is adsorbed. It is sufficient if the radioelement forms a sparingly soluble compound with one of the constituents of the adsorbing substance. Thus RaE is an isotope of bismuth,[2] and bismuth salts are not precipitated by sulphates but can be separated by carbonates. If now the solution containing the RaE is treated with barium salts and the barium precipitated as sulphate, the radioactive compound is left in solution; but if a carbonate is added it comes down with the barium. It is then a simple matter to separate the RaE from the barium by treatment with sulphuric acid. It is not even necessary to produce the precipitate in the solution—for instance, addition of previously prepared barium carbonate causes the adsorption of RaE.[3]

Radioactivity.—It is thus seen that the separation of the radioelements involves no new procedure; only when isotopes (p. 73) are

[1] *Ber.*, 1902, 35, 2285.   [2] Fajans and Beer, *Ber.*, 1915, 48, 700.
[3] Paneth and Horovitz, *Z. physikal. Chem.*, 1913, 89, 513.

present is a separation impossible by the ordinary methods of chemistry. The characteristic properties of this group of elements depend mostly on the instability of the nuclei of their atoms; the nuclei of the radioactive elements have an extraordinary tendency to break up and to hurl the fragments outwards with great energy. This emission of the fragments in the form of rays, which in their turn give ether waves when they strike other objects, is the most characteristic phenomenon of radioactivity.

Several different kinds of radiation can be emitted by radioactive substances. Each kind of radiation is characterised by its deflection in a magnetic field, its range and power of penetrating solid bodies. The α-rays (helium nuclei) and β-rays (electrons) are primary radiations, and more recently neutrons and positrons also have been recognised, largely through a study of artificial radioactivity (see p. 87). The γ-rays and the so-called recoil rays are secondary effects due to the action or production of the primary rays.

α-Rays.—The electrical charge (+) on the α-particle is twice as great as that on an electron and opposite in sign. That the α-particles have mass of the order of that of atoms can be determined from their deflection in a magnetic field. Their speed is also considerable and ranges initially from $1.5 - 1.8 \times 10^9$ cm./sec. They can be counted by allowing them to strike a surface covered with zinc blende, when they give rise to fugitive flashes which are easily visible through a magnifying glass in the dark. The whole path of these particles can be made visible if they are passed through a layer of supersaturated water vapour; the supersaturation is resolved by the charge on the particles, and the path can be photographed as a streak of mist. The form of the path has furnished valuable information on the structure of the atom, as mentioned on p. 2.

Ramsay and Soddy showed that helium was one of the products of the disintegration of radium,[1] and Rutherford and Royds[2] succeeded in showing that the α-rays contained helium. They placed some radium emanation in a thin sealed glass tube in a vacuum, and found that helium rapidly appeared in the vacuous space outside the tube, although ordinary helium was incapable of penetrating the walls of the sealed tube. The α-rays, which had passed through the walls of the tube, had given up their charge outside and formed helium, which gave its characteristic spectrum.

As the α-rays consist of material particles their flight is impeded by obstacles, and even gases are not penetrated by them to any great extent. The range of the α-rays in a gas depends on the nature of the gas and is inversely proportional to the pressure and directly proportional to the absolute temperature. These rays are stopped by solid bodies but can pass through thin layers on account of the

[1] *Proc. Roy. Soc.*, 1904, 73, 346. [2] *Phil. Mag.*, 1909, 17, 281.

enormous energy of their motion; it must be remembered also that "solid" bodies are largely empty space. The impeding effect of a substance varies as the square root of its atomic weight; thus the rays penetrate hydrogen to four times the depth of penetration in oxygen. They are able to break up the nuclei of atoms which are in their direct path, with effects as described on p. 10. When only the electron layer is hit by the α-particles, which naturally occurs much more frequently, electrons are dislodged and the air around becomes ionised in consequence.

Other things being equal, the range of the α-particles in air is characteristic for each radioelement. At 15° and 760 mm. the shortest range is that of the rays from uranium, 2·37 cm.; while the longest is that of the thorium-C rays, 11·3 cm. Most of the rays, however, have a range of less than 6·5 cm. There is a connection between the range and the life period of the radioactive substance; the greater the range the more rapid is the disintegration of the radioelement, and the life of the substance can be calculated from the range with a fair degree of accuracy. The ranges of particles are given beneath the arrows in the table facing p. 72.

β-rays.—The properties of the β-rays are quite different from those of the α-rays. A magnetic field deflects them in the opposite direction to that taken by the α-rays, thus indicating that the β-rays carry a negative charge. The deflection of the β-rays is also much greater, and although it is constant for the same kind of ray it differs for rays from different substances. In general, the β-rays are not homogeneous, and deflection by a magnetic field gives rise to a spectrum, from which information may be gained about the phenomenon of nuclear isomerism (p. 90). Again, the mass of the particles in the β-rays is small compared with that of the α-particles, being at low velocities only $1/1845$ of the mass of the hydrogen atom. This mass is identical with that of the particles in the cathode rays of the Röntgen tube—in fact, both sets of particles are electrons, but those of the β-rays are distinguished by their greater velocity, which is never less than one-third of that of light, and may even amount to 99 per cent. of that velocity. These swiftly moving electrons easily penetrate solid bodies, but they are stopped by a layer of lead 2 mm. thick. The slower, less penetrative rays are known as "soft" rays, while those which penetrate more deeply are called "hard" rays. Here, again, there is a connection between the atomic weight of the obstacle and its obstructive power, though its effectiveness does not increase regularly with the atomic weight, and if the two properties are plotted as a graph a wavy curve is obtained, with the alkali metals at the crests, which is reminiscent of the atomic volume curve. Each trough in the curve, however, is shallower than the one which precedes it, while this effect is much less noticeable in the atomic volume curve.[1] The absorption of the β-rays

[1] Crowther, *Phil. Mag.*, 1906, 12, 379.

by molecules is an additive property of the atoms which compose them.

γ-Rays.—When the cathode rays strike a solid body (the anticathode) they give rise to vibrations in the ether known as Röntgen rays. In a similar manner the β-rays cause ether rays like the Röntgen rays; these are called γ-rays. As the β-rays originate from below the surface of the radioactive substance, this itself acts as an anticathode, so that γ-rays are among the direct products of radioactivity. The γ-rays do not appear except in conjunction with β-rays, and they vary with the quality of the latter radiation; those from radium penetrate more deeply than those from uranium, which in turn are more intense than those of actinium. The γ-rays have naturally no mass and are thus not deflected by magnetic or electric fields. This radiation is, however, very penetrating, and as the electrons given off by radioactive substances have a greater velocity than those produced in the Röntgen tube, the corresponding γ-rays are also much more active than the Röntgen rays; they are extremely hard and penetrate deeply into the tissues of the body, so that they are of great utility in medical treatment. While a sheet of lead 2 mm. thick stops both α- and β-rays, the γ-rays pass through such a screen almost unaffected, and can be obtained pure in this way. The γ-radiation from 30 mg. of radium only falls to 1/100 of its value after traversing 760 m. of air, and even then it can pass through a block of iron 30 cm. in thickness. These rays, however, produce only slight ionisation of the air through which they pass; they do not cause the disintegration of atoms, and the ionisation which results is only 1/100 of that caused by β-rays and 1/10000 of that produced by α-rays. The nature of the obstacle affects the absorption of γ-rays, and elements of medium atomic weight show a minimum quotient of absorption and density.

Recoil Rays.—These rays are the result of the liberation of the α- and β-rays from the radioactive atoms. As α- and β-rays are emitted with great velocity they produce a recoil velocity, just as a shell gives a recoil velocity to the gun it leaves. This velocity is in a direction opposite to that of the other rays, and the recoil rays thus consist of atoms from which the α- and β-rays have come, their masses being almost the same as those of the original atoms. These rays are therefore at once identified as the same as the canal rays of the Röntgen tube. If the recoil rays are allowed to strike a charged plate the disintegration product collects there; it finally becomes so concentrated that this method can be used for the isolation of the decomposition product.[1]

Chemical Action of the Rays.—When the various rays strike chemical compounds, these are decomposed very much as in photochemical reactions, the results being most similar to those produced by ultraviolet rays. The effect is, however, much more rapid and

[1] Hahn, *Verh. Deutsch. Physik. Ges.*, 1909, 11, 55.

far-reaching than that of light, and the α-rays are most effective, the γ-rays least so. The decomposition which results is not equivalent to the total energy of the rays producing it, but depends on the ionisation produced when the rays traverse the matter in their path. The reaction produced is independent of the thermal effect of the transformation; many of the reactions produced by radium, like those caused by light, are reversible, and hydrogen chloride or carbon monoxide can either be synthesised or decomposed by the action of the radiations.

The most important action of the rays from radium is that upon the air and on water vapour. Water is converted into oxygen and hydrogen, though ozone and hydrogen peroxide are also among the products, the latter from the action of the β-rays. Ozone is also formed from the air when the radiations traverse it, and for this reason paper and other materials kept in the neighbourhood of radium are destroyed. The hardening of paraffin and of rubber, the decomposition of stopcock grease with evolution of carbon dioxide, and the bleaching of colours are also caused by the rays. Some of the other effects are more strictly comparable to the action of light, e.g. the conversion of yellow phosphorus into the red variety, the development of colour in glasses—soda and manganese glasses become violet, while those containing potash or much iron are turned brown—but as the radiations from radium cause the changes to proceed much more rapidly than the action of ordinary light rays, many effects are produced which light fails to give. Among these are the formation of blue rock-salt (cf. p. 238), the conversion of the surface of diamonds into graphite, the development of a yellow colour in sapphires (an effect not produced with artificial stones), and in general the rapid production of colour changes in minerals of many kinds.

It is therefore not surprising that radium acts upon the skin with production of sores, which in part resemble burns and in part abscesses which heal very slowly, followed by atrophy and a tendency to cancerous growth. These effects, like those caused by X-rays, only appear some time after exposure. As diseased tissues are attacked more readily than healthy ones, it is possible, by careful treatment with radium, to destroy diseased parts of organs and permit healthy growth to take place. It has been shown by experiments on plants that small doses of radiation cause growth of tissue, and it is possible that the healing properties of radioactive springs are due to this effect.

It may also be mentioned that the radiations cause precipitation of the particles in colloidal solutions, but only when they are positively charged, as this action is due to the β-rays.

Disintegration Products.—The disintegration of the atoms of the radioactive elements is a consequence of the emission of α-rays or of β-rays, but the other kinds of radiation are without effect. The

α- and β-rays originate in the nucleus of the atom, which can be compared with an endothermic compound which has a pronounced tendency to decompose. There is, however, a great difference in the energy relations, and the energy of atomic disintegration is many times greater than that involved in ordinary chemical reactions. For example, the heat produced by the disintegration of radium is ten thousand times as great as that given out by the combination of an explosive mixture of oxygen and hydrogen of the same weight. It is not therefore very remarkable that the temperatures of a few thousand degrees, which are all that can be attained in ordinary experimental work, produce no noticeable change in the rate of disintegration of the radioelements, which involve energy changes of a totally different order. The relation between time and quantity decomposed is very significant: in equal times equal numbers of atoms of the same radioelement are decomposed. This relation is characteristic of reactions of the first order. The actual velocity coefficient varies a good deal for various radioelements, and the life period of a radioactive substance may be anything from a fraction of a second to several thousand years. The disintegration often gives products which are themselves radioactive, and which may have an even shorter life than the parent material. These in turn give rise to other products, so that in old radioactive preparations there is usually a mixture of different materials, which can be separated by the methods previously described. It is obvious that the pure substances will not remain pure for any length of time, and they sometimes decompose extraordinarily rapidly (cf. table facing p. 72).

Uranium shows these effects very clearly, and it was in the disintegration of this element that they were first elucidated. The life of the parent uranium and of the first disintegration product, UX, is so prolonged that their properties are not much affected by the appearance of disintegration products of the second generation. Natural uranium salts have to some extent the power of discharging electrically charged bodies and of ionising the surrounding air. If a natural uranium salt is extracted with water and ether (p. 64) a portion of the material remains in the aqueous layer, while the uranium (which has the more marked electrical properties owing to emission of α-rays) passes into the ethereal layer. The UX in the water gives only β- and γ-rays. The ether layer, however, develops a greater radioactive power, while the aqueous layer loses its power, but if the system is left for a few months both layers reach their original state. This is due to the production of UX from the uranium, and the UX in its turn is converted into even less active products. In old preparations an equilibrium is set up and the UX is formed from the uranium just as fast as it is itself disintegrated; the discharging power thus remains constant. The

curves in Fig. 22 show the increase in the activity of uranium and the decrease in activity of UX with lapse of time.

In thorium, again, the first product is very short-lived, while that formed from it is disintegrated less rapidly. This gives rise to more complex relations. The form of the activity curve, however, indicates the formation of an intermediate product. It is, however, more difficult to determine the life period of one of the radioelements in a system of this sort. As the reactions are unimolecular, the relation

$$N_t = N_0 e^{-\lambda t}$$

holds for the quantity of any one kind of atom (N_0 being the original quantity, N_t the quantity present after time t, and λ the fraction which is changed in unit time—the transformation constant).

The term mean life period indicates the number of atoms out of which
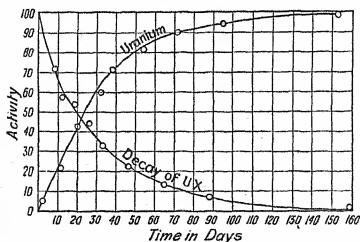
FIG. 22.—Variation in β-ray activity of U and UX.

one is disintegrated per day; but the time of existence of radioactive substances is more often estimated by the half-life period, being the time in which half the atoms are disintegrated, i.e. $\dfrac{N_t}{N_0} = \dfrac{1}{2}$. This constant, T, $= \dfrac{0.69315}{\lambda}$. The half-life period of UX, for example, is 24·6 days, i.e. after this time its radiation (β-rays) has fallen to a half of its original value. After a further 24·6 days the radiation falls to a quarter of the initial value, and after yet another 24·6 days to an eighth; thus, with periods of time in arithmetical progression, the radiation varies in geometrical progression. In the same way the activity of purified uranium increases until finally an equilibrium is reached in which the disintegration is exactly balanced by the further reactions which occur. In this equilibrium the ratio of uranium to UX must be constant, and a similar relation must hold for all products of U and of UX. Consequently, if a substance is found in old uranium compounds in a

constant ratio to the uranium content, it may be presumed that it is a disintegration product of uranium and is itself decomposing further. The radium in uranium minerals is present under these conditions, for in uranium minerals from ancient rocks the ratio of the quantity of radium to that of uranium is $3 \cdot 2 \times 10^{-7}$. This ratio is independent both of the nature of the mineral and of the absolute content of uranium, as seen in the following brief table:

Mineral.	Origin.	Per cent. U.	Per cent. Ra.	Ratio Ra/U.
Bröggerite . .	Norway	63.89	$2 \cdot 10 \times 10^{-5}$	$3 \cdot 29 \times 10^{-7}$
Pitchblende. .	Joachimsthal	46.11	1.48 ,,	3.21 ,,
,, . .	Cornwall	28.70	1.07 ,,	3.74 ,,
Gummite . .	Germany	17.37	0.58 ,,	3.34 ,,
Chalcolite . .	Portugal	0.724	0.024 ,,	3.35 ,,

Radium also reappears in uranium salts from which it has previously been completely removed, and it is thus a product of the decay of UX, itself derived from uranium. Other members of the series of disintegration products are ionium, which is intermediate between UX and Ra, and radon (radium emanation, niton), which is formed from radium. The chemical properties of these disintegration products are very different, in fact they usually belong to different groups in the periodic system; thus ionium is similar to thorium, radium to barium, and radon to xenon. The atomic weights of the products of decay differ from that of the parent substance when they are formed by the loss of α-rays (helium nuclei with double positive charges), but only slightly when the decay only produces β-rays (electrons).

The investigation of its disintegration products is the most fruitful way of determining the nature of a radioactive element. There are two of these disintegration series—that of uranium and that of thorium. The actinium series, which was at one time thought to be a separate series, is really part of the uranium series, forming a long branch chain. The table facing page 72 gives a summary of these series, and with each member is given its half-life period, the kind of radiation emitted (above the arrow) and the range of the α-particles in air in cm. (below the arrow). Some of the radioelements are analogous to, or isotopic with, more common elements, and this is also shown in the table by the group in which they are placed.

Decomposition of the Atom.—When an atom emits an α-particle (i.e. a doubly charged helium nucleus) its atomic weight diminishes by four units—the atomic weight of helium. Thus when uranium (A.W. 238.07) loses an α-particle, UX_1 (A.W. 234.1) is produced. As the helium nuclei which are expelled bear two positive charges, the remaining UX_1 falls into position in the periodic system two groups to the left of the parent element uranium, as there is a

difference of one in the positive charge on the nucleus (atomic number) in moving from one group into the next. As uranium is in the sixth group, UX_1, the residue after loss of four units of atomic weight and two positive charges, finds a place in the fourth group of the system ; its properties are actually found to be similar to those of thorium. This result may be stated quite generally : an element emitting α-rays passes into another element four units lighter in atomic weight and two units less in atomic number, and situate two groups to the left of the original element, in the periodic system (Russell-Fajans-Soddy displacement law). When the daughter element also gives α-rays the process is repeated. When the repetition of this process finally gives a rare gas of Group O, if this substance also emits α-rays the element formed therefrom is found to be in Group VI B. The atomic weight of protoactinium has now been determined as 231, which necessitates a revision of the atomic weights of elements derived from it [1] (see p. 83).

The consequences of the emission of β-rays are very different. As the mass of the electrons is very small, their loss does not affect the atomic weight of the element, but owing to their negative charge the effect on the atomic number of the element is opposite to that produced by the loss of α-particles—the position of the element in the periodic system is altered one group to the right, as each β-particle bears only unit negative charge. The emission of a β-ray gives a new element of almost the same atomic weight as the original one, but with an atomic number which is one greater than that of the parent element. Thus UX_1 gives UX_2, which is similar to tantalum in properties.

Comparison of the Disintegration Series.—In considering the table of the radioactive elements (facing this page) the question arises whether the sequence of disintegration is the same in the two series. There is a certain similarity at least in the middle portion of each series. The three "emanations" are similar in being gases, but their life periods are very different. They all give off α-rays, giving the "A" elements, ThA, AcA and RaA, all of which are characterised by a very brief existence, and by emission of α-rays to give the "B" elements. These are fairly long-lived, and give "C" elements by loss of β-rays. These again can emit either α- or β-rays with production of "C′" and "C″" elements respectively. The "C″" elements, again, give α-rays and D elements, but at this point the similarity ceases. In the same way, going left from the emanations, there is also a similarity of behaviour extending over several members, but again the beginnings of the three series are not comparable.

A connection between the life period and the atomic volume was established by St. Meyer [2]—the greater the atomic volume of an element in one of the series the shorter the life of the element. Fajans has found that for elements of the same atomic number the time of

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[1] von Grosse, *Proc. Roy. Soc.*, 1935, [A] 150, 363.   [2] *Ber. Wien. Akad.*, 1915, 249.
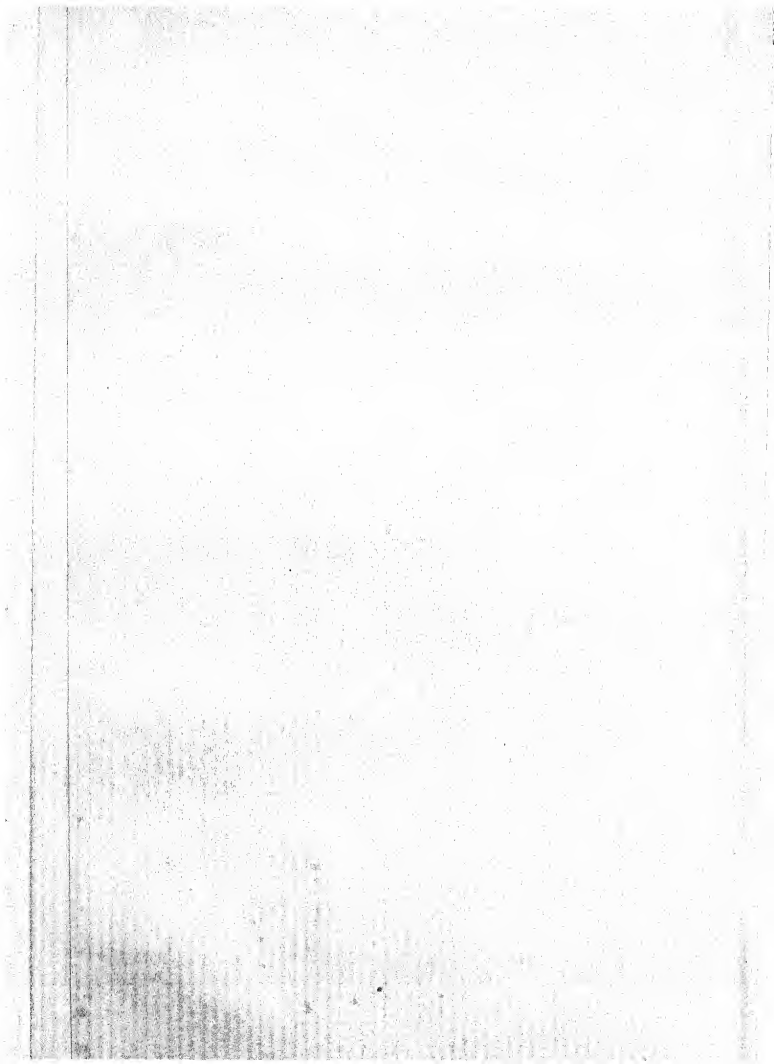
existence diminishes with increasing atomic weight when α-rays are given off, and increases with the atomic weight when β-rays lead to the next product.

Radioactivity is thus a property of elements of high atomic weight; the structure of their atoms is complex and they show a marked tendency to disintegrate. It would, however, be inaccurate to state that none of the other lighter elements are radioactive ; indeed, potassium, rubidium and samarium exhibit natural radioactivity (p. 84), while active isotopes of many of the lighter elements have been produced artificially (p. 87).

Isotopes

The series produced by the decay of a radioelement follows a zigzag path in the periodic system. Loss of an α-particle reduces the atomic number by 2, while the emission of an electron increases it by unity. It may be noticed, however, that UX_1, formed from uranium and having an atomic weight of 234·1, has thus the same atomic *number* as thorium of atomic weight 232·4. Both these elements should therefore occupy the same position in the periodic classification, though their atomic weights are different. This result is most curiously exemplified when an element gives out α-rays and its daughter element and the one after that in the series both give β-rays; this brings the fourth member of the series back into the same group as the original element but with an atomic weight diminished by four, *e.g.*:

		α		β		β	
	Th	$\longrightarrow$	MsTh$_1$	$\longrightarrow$	MsTh$_2$	$\longrightarrow$	RaTh
A.W.	232·1		228·1		228·1		228·1
Group	IV.		II.		III.		IV.

As a consequence of the emission of α- and β-rays in an irregular sequence the products of disintegration are scattered here and there in the lower part of the periodic system; in the end one product is usually found to occupy the same square as the ancestral element, although its atomic weight has become less owing to loss of α-particles. In this way a whole collection of elements can claim a single position in the periodic system, and all the squares after that occupied by thallium contain these collections of elements with the same atomic number but a different atomic weight. For instance, the square which contains lead really accommodates no less than seven different elements—the simpler definitions of an element need modification. These important relations were first observed by Soddy[1] and Fajans.[2] The latter referred to these groups of elements as pleïads—the lead pleïad, the thorium pleïad, etc. The single elements in these collections are called *isotopes* (as they occupy the same place). The table on the sheet facing p. 72 shows the groups into which the various

[1] *Chem. News*, 1913, 107, 97.　　　　　　　[2] *Ber.*, 1913, 35, 240.

radioactive products fall.[1] The atomic weights of the products can be deduced from the processes of formation from the parent elements given in the genealogical table. The radioactive substances are isotopic with the commoner elements at the base of the table. The effects of α- and β-radiations in the production of isotopes are clearly seen, and atomic numbers range only between 81 and 92. The last two series of the periodic system therefore include the elements given in the table.

Isotopes differ from one another in the mass and structure of their nuclei but not in the net positive charge thereon nor in the number of electrons in the outer electron layers. They thus show identity in all properties which depend on the outer electron layers, and not only their chemical properties but also their spectra, magnetic susceptibility, etc., are exactly the same for all the isotopes in a given position in the periodic system. Even the tendency to ionisation is the same in all the members of a given pleiad.[2] Isotopes cannot therefore be separated from one another by the usual methods of chemistry, and separation is only possible by making use of properties which depend on the atomic weight.

The first indication of the existence of isotopes was in the collection of elements in the lead position (No. 82) in the periodic system. The radioactive products of this atomic number are formed by loss of α- and β-particles from thorium (A.W. 232.12) or uranium (A.W. 238.07). Subtracting multiples of four from these numbers to get a figure nearest to 207.2, the atomic weight of pure lead, the figure 208.4 is obtained from thorium and 206 from uranium. Hence lead formed from thorium has a higher atomic weight than ordinary lead, while that from uranium has a lower atomic weight. This deduction has been amply verified. Richards and Lembert[3] investigated the lead found in various uranium minerals, and discovered that the atomic weight of lead from these sources was less than that from other ores. Thus lead from carnotite showed A.W. = 206.6, from uraninite A.W. = 206.35, but that from thorianite, which contains both uranium and thorium, gave A.W. = 206.8. Lead obtained from a mineral rich in thorium (30 per cent.) but poor in uranium gave the atomic weight 207.9. All these different kinds of lead were chemically indistinguishable, showing that the electron shells were unaffected by the alteration in atomic weight

Determinations of the atomic weights of lead from various sources have given a very beautiful example of the support which the classical method, based on ratios arrived at by the precipitation of an insoluble salt, receives from the recently perfected technique utilising mass spectra (p. 76). Thus the atomic weight of non-radiogenic lead, based on the precipitation of silver chloride or bromide from lead chloride

[1] Cf. also Soddy, *J. Chem. Soc.*, 1919, 115, 1.
[2] v. Hevesy and Paneth, *Monatsh.*, 1915, 36, 75.
[3] *Z. anorg. Chem.*, 1914, 88, 429.

or bromide solutions, was found by various workers to be between 207·19 and 207·21. Aston examined the mass spectrum of lead tetramethyl, $Pb(CH_3)_4$, prepared from ordinary lead, and found isotopes of the mass numbers and abundances shown; the relative abundances are arrived at from photometric measurements of the intensities of the mass spectral lines.

| Mass Number | . | 203, | 204, | 205, | 206, | 207, | 208, | 209, | 210 |
| % abundance | . | 0·04, | 1·50, | 0·03, | 27·75, | 20·20, | 49·55, | 0·85, | 0·08 |

This gives a mean mass number of 207·19. The packing fraction (see p. 30) of lead is probably zero, so that the atomic weight arrived at by this method is 207·19. Radiogenic leads were examined in the same way, with the following results:

Source of Lead.	Atomic Weight [1] (Chemical).	Isotopes [2] 206, 207, 208.	Mean Mass Number.
Pitchblende (Belgian Congo) . .	206·048	%93·1, 6·7, (0·02)	206·067
Pitchblende (Ontario)	206·195	85·9, 8·3, 5·8	206·199
Thorite (Norway)	207·90	4·6, 1·3, 94·1	207·895

Other examples of isotopy have since been studied. Thus thorium (A.W. 232·12) is isotopic with ionium (A.W. 230·2), and although the latter has not been obtained in the pure state it depresses the atomic weight of thorium with which it is mixed to 231·5. The isotopes of lighter elements are discussed on the following pages.

As the form of the outer electron shells is the same for all isotopes with a given atomic number, the atomic volume is also the same, and as the atomic weight is different the density should also show differences. The various isotopes of lead actually show the same atomic volumes but different densities:

Pb of A.W. .	207·2	A.V. .	18·277	d. .	11·337
,, ,, ,, .	206·3	,, .	18·274	,, .	11·289

In the same way the solubility of compounds of isotopes must be the same as long as only the number of dissolved molecules is considered, but as the molecules differ in weight the densities of the saturated solutions are different. For instance, the density of a saturated solution of ordinary lead nitrate at 24·45° is 1·444499, while when the lead nitrate is made from pitchblende the density is 1·443586.

Isotopes may conveniently be represented by writing the usual symbol of the element and immediately preceding it by two numerals, the upper one giving the weight of the atom relative to hydrogen as

[1] Hönigschmid, *Z. Electrochem.*, 1919, **25**, 91; Hönigschmid and Birckenbach, *Ber.*, 1923, **56**, 1837; Baxter and Bliss, *J. Amer. Chem. Soc.*, 1930, **52**, 4951.

[2] Aston, *Nature*, 1929, **123**, 313; 1932, **129**, 649; *Proc. Roy. Soc.*, 1933, **140** A, 535.

unity, the lower numeral being the atomic number. Thus $_1^1\text{H}$ represents hydrogen of mass 1, atomic number 1, whereas $_1^2\text{H}$ is the heavier isotope (deuterium); similarly $_5^{11}\text{B}$ and $_5^{10}\text{B}$, $_{82}^{206}\text{Pb}$ and $_{82}^{208}\text{Pb}$ are isotopes of boron and of lead. The production of lead from uranium by loss of α-particles ($_2^4\text{He}$) and β-particles ($_{-1}^0\text{e}$) can then be represented:

$$_{92}^{238}\text{U} - 8_2^4\text{He} - 6_{-1}^{\;0}\text{e} = {}_{82}^{206}\text{Pb}$$

and from thorium thus:

$$_{90}^{232}\text{Th} - 6_2^4\text{He} - 4_{-1}^{\;0}\text{e} = {}_{82}^{208}\text{Pb}$$
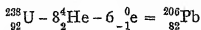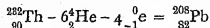
the numerals on the right hand side being arrived at by the separate summation of the upper or lower numerals on the left-hand side of the equation (see p. 10).

Positive Ray Analysis.—The most successful method of detecting the existence of isotopes is that involving the use of positive ray analysis. A study of band or molecular spectra has also given very valuable evidence. The canal rays are recoil rays which consist of atoms moving in the opposite direction to the cathode rays; they are deflected by magnetic and electric fields to an extent which depends on their mass and velocity. Using this method, J. J. Thomson, F. W. Aston, K. T. Bainbridge and other workers have been able to show that many elements hitherto supposed to be simple are really mixtures of isotopes.[1] In Thomson's "parabola" method, mass rays after deflection in magnetic and electric fields fall on a photographic plate; the image produced by particles of equal mass, but different velocities, is a parabola, the *latus rectum* of which is inversely as the mass of the positive ray. In Aston's apparatus, the direction of application of the magnetic field is at right angles to that in Thomson's apparatus, the direction of application of the electric field being the same in each; all particles of the same mass are brought to a common focus, which is recorded as a line on a photographic plate. The images produced by particles of different masses follow an approximately linear distribution on the photographic plate. In Bainbridge's procedure, the particles are made homogeneous in velocity and are then deflected in a magnetic field. The images are strictly linear with mass.

The elements in the table on p. 77 have been shown by their mass spectra to be composite, the letters a, b, c, d, etc., indicating the relative quantities of the various atoms in the naturally occurring element.

Aston remarks that elements of odd atomic numbers have at most two isotopes. The following elements have been shown to be "pure" by the positive ray method: He, Be, F, Na, Al, P, Sc, V, Mn, As, Y, Nb, I, Cs, La, Pr, Tb, Ho, Tm, Ta, Au, Bi, Th.

It is remarkable that the atomic weights of the individual elements in the mixtures of isotopes all approach whole numbers, if $^{16}\text{O} = 16 \cdot 000$. The mixtures of isotopes which form the naturally occurring elements do not have whole number atomic weights, as those determined by the ordinary chemical methods are the weighted means of the atomic weights of the isotopes which they contain.

TABLE OF ISOTOPES

Element.	Masses of Isotopes.
H . . .	1a, 2b
Li . . .	6b, 7a
B . . .	10b, 11a
C . . .	12a, 13b
N . . .	14a, 15b
O . . .	16a, 17c, 18b
Ne . . .	20a, 21c, 22b,
Mg . . .	24a, 25b, 26c
Si . . .	28a, 29b, 30c
S . . .	32a, 33c, 34b
Cl . . .	35a, 37b
A . . .	36b, 38c, 40a
K . . .	39a, 40c, 41b
Ca . . .	40a, 42c, 43d, 44b, 46f, 48e
Ti . . .	46b, 47c, 48a, 49d, 50e
Cr . . .	50c, 52a, 53b, 54d
Fe . . .	54b, 56a, 57c, 58d
Co . . .	59a, 57b
Ni . . .	58a, 60b, 62c, 64e
Cu . . .	63a, 65b
Zn . . .	64a, 66b, 67d, 68c, 70e
Ga . . .	69a, 71b
Ge . . .	70c, 72b, 73d, 74a, 76e
Se . . .	74f, 76c, 77e, 78b, 80a, 82d
Br . . .	79a, 81a
Kr . . .	78f, 80c, 82c, 83d, 84a, 86b
Rb . . .	85a, 87b
Sr . . .	84d, 86b, 87c, 88a
Zr . . .	90a, 91d, 92b, 94c, 96e
Mo . . .	92d, 94e, 95c, 96b, 97g, 98a, 100f
Ru . . .	96a, (98), 99f, 100d, 101b, 102a, 104c
Rh . . .	101b, 103a
Pd . . .	102f, 104e, 105c, 106a, 108b, 110d
Ag . . .	107a, 109b
Cd . . .	106g, 108h, 110c, 111e, 112b, 113d, 114a, 116f
In . . .	113b, 115a
Sn . . .	112h, 114i, 115j, 116c, 117e, 118b, 119d, 120a, 122g, 124f
Sb . . .	121a, 123b
Te . . .	122f, 123g, 124e, 125d, 126c, 128b, 130a
Xe . . .	124h, 126h, 128g, 129a, 130f, 131c, 132a, 134d, 136e
Ba . . .	130f, 132g, 134e, 135d, 136c, 137b, 138a
Ce . . .	140a, 142b
Nd . . .	142a, 143d, 144b, 145e, 146c, 148f, 150g
Sa . . .	144g, 147c, 148e, 149d, 150f, 152a, 154b
Eu . . .	151a, 153a
Gd . . .	152f, 154c, 155b, 156a, 157c, 158a, 160d
Dy . . .	158e, 160d, 161c, 162b, 163b, 164a
Er . . .	162f, 164e, 166a, 167c, 168b, 170d
Yb . . .	168g, 170f, 171e, 172b, 173c, 174a, 176d
Lu . . .	175a, 176b
Hf . . .	174f, 176e, 177c, 178b, 179d, 180a
W . . .	180e, 182c, 183d, 184a, 186b
Re . . .	185a, 187a
Os . . .	184g, 186e, 187f, 188d, 189c, 190b, 192a
Ir . . .	191b, 193a
Pt . . .	192e, 194b, 195a, 196c, 198d
Hg . . .	196g, 197h, 198e, 199c, 200b, 201d, 202a, 203i, 204f
Tl . . .	203b, 205a
Pb . . .	204d, 206b, 207c, 208a
U . . .	234c, 235b, 238a

It often happens that a "pure" element is not the only one with that atomic weight; this can be seen from the following table of isobaric atoms:

A^{40} Cr^{54} Zn^{70} Ge^{74} Ge^{76} $Se^{78, 80, 82}$ Rb^{87} $Zr^{92, 94}$ Kr^{86} $Mo^{96, 98, 100}$

These discoveries throw new light on the lack of a simple relation between the atomic weights and the atomic numbers. In four places in the periodic system it is necessary to arrange elements in the reverse order of atomic weight in order that the sequence may conform to that of atomic number and of other properties; potassium (A.W. 39·096) is placed after argon (39·944); nickel (58·69) after cobalt (58·94); iodine (126·92) after tellurium (127·61), and protactinium (231) after thorium (232·12). It is now clear that the same atomic number, and hence the same place, may be claimed by a number of elements of differing atomic weight. It is only the structure of the outer layers of the atom, and not its weight, which determines most of its chemical properties and hence its position in the periodic system. This position is usually assigned by observation of the more superficial properties of the element, and often gives but little indication of the full chemical properties. If a radioactive element which is present in minute quantities is recrystallised with an inactive element and is found in the same proportion in crystals and mother-liquor, it may be taken to be an isotope of the inactive element.

Separation of Isotopes.—Differences in density can be applied to the separation of isotopes; for instance, the rate of diffusion of a gas is inversely proportional to the square root of its molecular weight, so that heavier isotopes diffuse less readily than lighter ones. Harkins and Mortimer[1] succeeded in separating two fractions of mercury which differ by 0·2 in atomic weight.

Brönsted and v. Hevesy[2] separated mercury and chlorine into fractions of different density by careful distillation. Similarly, Aston has effected a separation of the isotopes of neon by applying the method of effusion.[3] G. Herz[4] has so far improved the apparatus that he has been able to effect a separation of the isotopes of neon, in which the proportion is 9:1. In eight hours a mixture containing about equal parts of the isotopes was obtained, the atomic weight going down from 21·18 to 21. A lighter fraction was also obtained in which only 1 per cent. of the heavier isotope was present. Boron from various sources gives different at. wts. (California 10·840, Tuscany 10·825, Asia Minor 10·818), indicating a variation in the proportion of the isotopes present.[5] The hydrogen isotope of mass 2 accumulates in the residual water left on electrolysis[6]; ordinary hydrogen contains 1 part in 5000 (see p. 159).

Quantitative studies on the relative masses and abundances of isotopes have proved of great value in the determination of atomic weights, and also led to the discovery of heavy hydrogen. In the

[1] *Phil. Mag.*, 1926 [vii], 6, 601.   [2] *Nature*, 1920, 106, 144.
[3] *Phil. Mag.*, 1920, 38, 713.   [4] *Naturwiss.*, 1932, 20, 493.
[5] Briscoe and collaborators, *J. Chem. Soc.*, 1925, 127, 150, 696.
[6] See *Nature*, 1933, 132, 536; Urey, Brickwedde and Murphy, *Physical Review*, 1932, 40, 1.

latter connection, Aston (1927) determined the following ratio by means of the mass spectograph

$$\frac{\text{Mass H}}{\text{Mass O}} = \frac{1 \cdot 00778}{16 \cdot 0000}$$

which is in complete agreement with the values found from the combining ratios of oxygen and hydrogen and also from the relative densities of the gases, corrected to ideal conditions.

This complete agreement was upset by the discovery of Giauque and Johnston[1] that ordinary oxygen contains not only $^{16}_8O$, but also $^{17}_8O$ and $^{18}_8O$, the relative abundance of the three isotopes in atmospheric oxygen being[2]:

$$^{16}O : {}^{17}O : {}^{18}O = 3150 : 1 : 5$$

The atomic weight of "mixed" or "chemical" oxygen, taking $^{16}O = 16 \cdot 0000$ is $\dfrac{3150 \times 16 + 1 \times 17 + 5 \times 18}{3156} = 16 \cdot 0035$. The atomic weight of hydrogen, determined by chemical means, referred to $^{16}O = 16 \cdot 0000$, is therefore $1 \cdot 00778 \times \dfrac{16 \cdot 0035}{16 \cdot 000}$, i.e. $1 \cdot 00799$.

This discrepancy of 2 parts in 10,000 between the two sets of determinations might be due to the presence of an isotope ^2_1H, hitherto undetected, present to the extent of 1 part of ^2_1H in 5000 parts of ^1_1H. This led Urey, Brickwedde and Murphy[3] to examine the Balmer spectrum of the residue remaining after the evaporation of a large quantity of liquid hydrogen; the spectrum showed the usual lines and in addition, a series of faint lines, which agreed exactly in position for those calculated for ^2_1H. The value found by Aston has since been changed, but the careful examination of a possible cause of the discrepancy which existed has led to one of the most striking developments in modern chemistry, the discovery of heavy hydrogen.

Differences in the properties of isotopes of an element are usually small, but in the case of ^1_1H and ^2_1H or deuterium (D), there are marked differences as shown in the following table[4]:

	H	D
Boiling point . . .	$20 \cdot 38°$ K	$23 \cdot 6°$ K
Melting point . . .	$13 \cdot 95°$ K	$18 \cdot 59°$ K
Molecular volume at m.pt. .	$26 \cdot 15$	$23 \cdot 15$
Heat of fusion (cals./mol.) .	28	47

D_2 is generally less reactive chemically than H_2 (see p. 159), but atomic protium and deuterium are equally reactive, e.g. H_2 reacts with N_2O at various surfaces, such as Ni, about twice as fast as does D_2,

[1] *Nature*, 1929, **123**, 318.   [2] Mecke and Childs, *Zeit. f. Physik.*, 1931, **68**, 362.
[3] *Physical Review*, 1932, **40**, 1.
[4] For a general discussion on deuterium, see *Z. Electrochem*, 1938, 44.

but the rates of the atomic reactions, $H + N_2O \longrightarrow N_2 + OH'$ and $D + N_2O \longrightarrow N_2 + OD'$ are equal.[1]

Tritium, $_1^3H$, which may be present in minute quantities in ordinary hydrogen, has been produced by bombarding a target of ND_4Cl or D_3PO_4 with accelerated deuterons (see p. 86):

$$_1^2D + _1^2D \longrightarrow _1^1H + _1^3T.$$
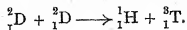
The determination of atomic weights, from data on isotopes, though less spectacular, is of great importance and has been referred to in connection with the determination of the atomic weight of lead (p. 75). As a further example, amongst many others, the atomic weight of carbon will be dealt with. Until recently, the accepted atomic weight of carbon was 12·00, referred to the chemical standard of oxygen = 16·0000. This value was based on ratios determined by such reactions as the conversion of Na_2CO_3 to $NaBr$ and to $AgBr$, and a knowledge of the atomic weights of sodium, silver and bromine, arrived at largely by the classical researches of Richards and his co-workers. The value was also obtained by determining the gaseous density of suitable carbon compounds, and by applying corrections, based on the measured compressibilities of the gases, so that "ideal" relative densities at zero pressures could be computed; under those conditions, Avogadro's hypothesis is taken to be accurate.

The discovery, by the methods of band spectroscopy, of $_6^{13}C$ present with $_6^{12}C$ showed that the accepted chemical value must be too low. Baxter and Hale[2] redetermined the atomic weight of carbon by the combustions of the hydrocarbons, chrysene, pyrene, triphenylbenzene and anthracene and found the value $C = 12·009$. This value is in close agreement with the value arrived at by Woodhead and Whytlaw-Gray,[3] who prepared and purified carbon monoxide with great care, and determined the corresponding pairs of pressures which must be applied to correspond to equal weights of CO and O_2 in a fixed volume; the values at 19·8° C are:

		Approximate Pressures.		Ratio Uncorrected.	Corrections.	Ratio Corrected.
		O_2	CO			
I	.	181·9	207·8	0·87535₅	− 0·000123	0·87523
II	.	361·9	413·5	0·87524₇	− 0·000112	0·87514
III	.	572·3	654·0	0·87509₈	− 0·000099	0·87500

The corrections applied were based on changes in volume of parts of the apparatus with changed pressure.

From these ratios the limiting value at zero pressure is arrived at

[1] Melville, *J. Chem. Soc.*, 1934, 797.   [2] *J. Amer. Chem. Soc.*, 1936, 58, 510.
[3] *J. Chem. Soc.*, 1933, 846.

by linear extrapolation, plotting ratio against pressure of gas. The values obtained are

	Limiting Ratio.	Molecular Wt. CO $^{16, 17, 18}O = 16\cdot0000$.
From I and II . . .	0·87533	28·010(6)
,, I ,, III . .	0·87534	28·011(0)
,, II ,, III . .	0·87537	28·011(8)

The internationally accepted value for C is now changed from the earlier value of 12·00 to 12·010.

The heavy nitrogen isotope, ^{15}N, has been concentrated[1] by the exchange reaction between NH_3 and $(NH_4)_2SO_4$. Partial separation of isotopes has also been accomplished by fractional distillation; thermal diffusion, in which the thermal effect is augmented by the effects of convection[2]; and by utilisation of chemical differences such as rate of base exchange in zeolites.

The more Important Radioactive Substances

The special properties of some more important radioactive elements will now be described. Radium and its emanation, actinium and mesothorium will be taken as typical examples.

Radium is found not only in the minerals from which it is usually obtained but also widely distributed throughout the earth's crust. It is found in all rocks, though often only in very small quantities, and the water of the ocean does not contain less than 20,000 tons of radium metal, but the concentration is too low for the extraction of the radium to be a practicable proposition. Radium is found in springs less frequently than its decomposition product—radium emanation.

Radium is isolated from pitchblende by taking advantage of its similarity in properties to the alkaline earths. The mineral contains a large number of different elements besides uranium; after opening up, it is digested with sulphuric acid when a residue of the sulphates of barium, calcium and lead, together with silica, is obtained. After conversion into carbonates and finally into chlorides (or better, bromides) the lead is separated, largely as lead chloride and the remainder as lead sulphide. Iron and alumina are then precipitated with ammonia, and the calcium chloride extracted with concentrated hydrochloric acid, in which the other halides are insoluble. Finally, the mixture is subjected to a process of fractional crystallisation similar to that used for the rare earths (p. 433). The radium bromide accumulates in the least soluble fractions, the barium bromide in the more soluble portions. In this way about one gram of $RaBr_2$, $2H_2O$ can be obtained from 10,000 kg. of Joachimsthal pitchblende.

Metallic radium can be obtained by Ebler's method,[3] which consists

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[1] Urey, Fox, Huffman and Thode, *J. Amer. Chem. Soc.*, 1937, 59, 1407.

[2] For a summary, see *Ann. Rep. Chem. Soc.*, 1938, 35, 134 ; 1940, 37, 153.

[3] *Ber.*, 1910, 43, 2613.

in decomposing the azide $Ra(N_3)_2$ by heating to 180°-250° (see p. 663). It was also obtained as a silvery white metal by Curie and Debierne,[1] by decomposing the amalgam obtained by the electrolysis of solutions of radium salts with a mercury cathode. The mercury distils off at 400°-700°, and the radium which is left behind melts at 700° and vaporises at a slightly higher temperature. It is thus more volatile than barium, in the same way that caesium is more volatile than rubidium.

The metal blackens at once in the air owing to formation of a nitride. The salts can be more readily preserved, especially when they are pure—the freedom of the radium salt from barium can be judged by its permanent white colour, which is lost when some barium is still present. Even pure radium salts decompose in time; the bromide becomes coloured and gives off bromine and water, but the residue contains all the radium. Glass vessels are preferable to those of silica for keeping radium compounds, as the latter are rapidly rotted.

Radium, being the heaviest of the alkaline earth metals, forms the least soluble sulphate of that series (100 g. water dissolve 0·14 mg. at 20°). Most of its salts, indeed, are less soluble than the corresponding barium salts, but its hydroxide, following the sequence of solubilities of hydroxides of the group, is more soluble than baryta. Radium gives an intensely red flame coloration which, even in low concentrations, masks the colour due to barium. In the electromotive series radium lies between sodium and barium.

Radium chloride loses its water below 200° and melts at yellow heat to a liquid which solidifies to a glassy mass. The solidified melt has the property of shining with a strong bluish-violet light, which the hydrated salt lacks; the light is so powerful that it can be seen in daylight. This luminosity is lost in the presence of water, especially when the salt is dissolved.

The production of heat from one gram of metallic radium, when the decomposition products are retained, is 132·3 cals. per hour. Under these conditions the α- and β-rays are almost completely resolved into heat effects, but the γ-rays are only transformed to the extent of 18 per cent. This great liberation of energy, while the amount of radium lost is so small as to defy detection, is only explicable by the long life-period of the radium. The half-life period is 1690 years and the energy effect is further increased by the retention of solid products of decomposition in the mass. The number of α-particles emitted per gram of Ra per second is $3\cdot7 \times 10^{10}$, and their range in air at 15° is 3·4 cm.

One of the most interesting products of the decay of radium is its emanation, the element *radon*. It results from the loss of an α-particle by the radium atom, and the helium formed when it is produced was the first example of a new element being formed by radioactive change (Ramsay, Rutherford). The emanation is a gas and fills the vessel con-

[1] *Compt. rend.*, 1910, **151**, 523.

taining the radium, and as it rapidly decomposes into other radioactive elements with emission of strong recoil rays the walls of the containing vessel become covered with this "active deposit." Radon is condensed in liquid air to a colourless liquid of boiling point $-85°$, and as its critical temperature is $105.5°$ it is readily separated from the more difficultly liquefiable helium. The best way to collect the radon from a radium salt is to dissolve the salt in water and let it stand, when the gaseous products remain in solution. On boiling, the radon, helium and a quantity of detonating gas formed by the decomposition of the water are driven off. After sparking the hydrogen-oxygen mixture the radon is separated from the helium by fractional liquefaction. The molecular weight of radon was found to be 222 both by the diffusion method and by weighing (Ramsay and Whytlaw-Gray). Its chemical properties are similar to those of the other rare gases. The solubility in water is: $0°$, 0.507; $39.1°$, 0.160; $100°$, 0.0, but it is more soluble in organic solvents—45 times as soluble in toluene and even more soluble in carbon disulphide. It forms colourless crystals at low temperatures, and these, like the liquid, shine in the dark with a strong bluish light, which becomes yellower in time. The spectrum of radon in the Geissler tube shows numerous lines in the green and violet and is quite different from that of radium.

After radium itself *mesothorium* is the most important substance in the applications of radioactivity. This element, of which the origin and destiny are shown in the table facing p. 72, is left in solution when compounds of the parent element thorium are precipitated with ammonia. As it is isotopic with radium it can be removed from the solution by adding barium salts and precipitation as sulphate. It differs from radium in decomposing more rapidly, giving first a more active element and then one which is less active. The activity of mesothorium thus increases for 3.2 years, when it is one and a half times its original value, and then decreases again till it reaches the initial value in 10 years, and after 20 years has only half that power.

None of the members of the actinium series has attained any great importance, although, after radium, protactinium is most readily obtained in some quantity, for a ton of pitchblende gives some 72 mg. protactinium —about a third of the quantity of radium.[1] Protactinium, the parent substance of actinium and the eka-tantalum of Mendeléev, is left behind in the residue containing tantalic acid which remains when the ore is treated with concentrated nitric acid. It is separated by the application of the knowledge that from its position in the periodic system it is more basic than tantalum. It is therefore precipitated from the residues containing tantalum by means of phosphates; it then contains only zirconium and hafnium, from which it is readily separated (A. v. Grosse[2];

[1] Hahn and Meitner, *Ber.*, 1921, 54, 69.
[2] *J. Amer. Chem. Soc.*, 1930, 52, 1742; *Ind. Eng. Chem.*, 1935, 27, 422.

Graue and Käding [1]). It is finally separated as K_2PaF_7, which can be converted to Pa_2O_5 by first evaporating with sulphuric acid, then precipitating by ammonia and igniting. By this procedure, v. Grosse [2] determined the atomic weight, Pa, 230.6 ± 0.5. Thorium, which precedes protactinium, has atomic weight 232.1 and a fourth anomaly in order of atomic weights is therefore added to the three already known (see p. 28). The compounds of protactinium resemble those of tantalum, but the resemblances are less close than those between barium and radium.

Actinium is slowly produced from protactinium. This substance is found only in uranium minerals and never in thorium minerals. Actinium resembles the more basic of the rare earths and is separated with them from the minerals, mostly as oxalate; the solubility of actinium oxalate is rather greater than that of the oxalates of the cerium earths. Actinium emanation has a much shorter life than the other emanations.

Potassium and rubidium show very faint β-radioactivity, the half-life periods being 1.9×10^9 years for K, and 5×10^{10} years for Rb. The question as to which potassium isotope is responsible for the activity has received considerable attention. Hevesy and Paul [3] effected a partial separation of the isotopes by distillation and concluded that ^{39}K did not carry the activity; moreover, the increase in activity of the heavier fraction was less than the increase in concentration of ^{41}K, so that this isotope was eliminated. ^{42}K has been produced artificially and decays with a half-life period of 16 hours, and since still heavier isotopes would be expected to have even shorter half-life values, only ^{40}K remains as the radioactive isotope. Separation of the isotopes by means of the mass spectrograph has confirmed the activity of this isotope, while further corroboration has been obtained from the analysis of ancient potassium rocks. If $^{41}_{19}K$ were responsible for β-activity, $^{41}_{20}Ca$ would be formed, and would accumulate. Aston [4] found no evidence of ^{41}Ca in Richonich pegmatite or Norwegian biotite. The abundance of ^{40}K (1 in 8500) would lead us to expect a greater activity in ordinary potassium, so that the disintegration must be of abnormally low probability.

The radioactivity of rubidium is the property of the $^{87}_{37}Rb$ isotope; this conclusion is based on the appearance of $^{87}_{38}Sr$ in the old Rb minerals, e.g. lithium mica.

Samarium shows an exceedingly weak α-activity, but which isotope is responsible has not been determined.

Nuclear Disintegration.—Reference has already been made to Rutherford's discovery of the proton in the reaction $^{14}N(\alpha, p)^{17}O$. Of the two reasonable courses which this reaction might follow:

$$^{14}_{7}N + {}^{4}_{2}He \longrightarrow {}^{13}_{6}C + {}^{4}_{2}He + {}^{1}_{1}H,$$
$$^{14}_{7}N + {}^{4}_{2}He \longrightarrow {}^{17}_{8}O + {}^{1}_{1}H$$
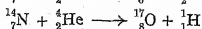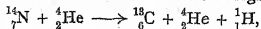
[1] Angew. Chem., 1934, 47, 650.   [2] Proc. Roy. Soc., 1935, [A], 150, 363.
[3] Z. physikal. Chem., 1931.   [4] Nature, 133, 869 (1934).

the former would give, after collision, two cloud tracks in the Wilson cloud chamber, while the latter would give only one. Photographs show that the α-particle track disappears and only one new track appears besides that of the recoil atom. The nature of the new particle, which is more energetic than the original bombarding particles, was deduced from its behaviour in the magnetic field and from the ratio of its charge to its mass.

It is clear, therefore, that the α-particle is captured by the nucleus of the nitrogen atom, which then disintegrates instantly. In many other cases the new nucleus is metastable and disintegrates exponentially with time (see p. 87). An α-particle, in general, can enter a nucleus only if it possesses sufficient energy to overcome the electrical repulsion. This "potential barrier" increases with increasing atomic number, so that only the nuclei of the lighter elements are penetrated by α-particles of ordinary energy. Sometimes, however, α-particles of lower energy than that required to overcome the potential barrier may effect entry into the nucleus, provided that they possess certain exact energies; this is called "resonance entry" or "resonance capture." Thus α-particles must possess an energy of about 6·5 million electron volts (M.e.v.) to overcome the potential barrier of the magnesium nucleus, but particles of energies 5·7 or 6·3 M.e.v. can effect resonance entry.

If the nitrogen in Rutherford's experiment is replaced by hydrogen, deuterons are obtained :

$$_1^1\text{H} + {}_2^4\text{He} \longrightarrow {}_1^2\text{D} + {}_2^3\text{He}.$$
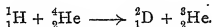
The helium isotope ^{3}He is formed in other disintegration processes, e.g. if trideuterophosphoric acid is bombarded with deuterons

$$_1^2\text{D} + {}_1^2\text{D} \longrightarrow {}_2^3\text{He} + {}_0^1\text{n}$$
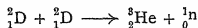
and there are traces in ordinary He.

Chadwick discovered that the α-particles from polonium ejected from beryllium massive particles of zero charge, which later were shown to be neutrons (see p. 2) formed according to the reaction $^9\text{Be}(\alpha, n) {}^{12}\text{C}$. The yield of neutrons is about 30 per million α-particles; many of the lighter elements react in a similar way, but the yield of neutrons is smaller still. Neutrons may be obtained also from deuterium, beryllium, etc., by utilising the "nuclear photoelectric effect"

$$_1^2\text{D} + h\nu \longrightarrow {}_1^1\text{H} + {}_0^1\text{n}$$
$$_4^9\text{Be} + h\nu \longrightarrow {}_4^8\text{Be} + {}_0^1\text{n}.$$
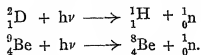
Consideration of the energy balance in the first of these reactions enables the mass of the deuteron to be calculated as 2·0144, and that of the neutron as 1·0084. (The mass of the proton is 1·0082.)

There are thus available four kinds of particles, which, by virtue of their atomic size and huge energy, can effect many nuclear disintegrations—α-particles, protons, deuterons and neutrons. As produced

in the reactions discussed above, these particles possess energy sufficient only to disrupt the lighter nuclei, although the neutrons, having no charge, are more effective than charged particles of comparable energy. In recent years, however, several attempts to accelerate charged particles by means of powerful electric fields have culminated in the development of the cyclotron, for which credit is due to E. O. Lawrence of the University of California. The cyclotron consists of two hollow D-shaped electrodes, to which is applied an alternating potential difference. The charged particles are produced in a gap between the D's and drawn rapidly inside one of the electrodes, where, of course, the electric field is virtually zero. A strong magnetic field is so arranged that the particles are deflected inside the electrode in a semicircular path and thus directed into the gap between the electrodes again. The frequency of the p.d. and the magnitude of the magnetic field are so adjusted that at the moment the particles re-enter the gap the direction of the electric field reverses, so that the particles are drawn into the other D and the whole process repeated. Each time a particle crosses the gap it acquires a further increment of energy, and a corresponding increase in linear momentum. Now, in the magnetic field the angular momentum is constant, so that with each successive deflection the particles describe larger semicircles, until they ultimately reach the circumference of one of the D's. Here a slit is arranged and the particles, leaving the cyclotron tangentially, are allowed to impinge normally on the target. Using accelerating voltages of only 8-10,000 volts and a frequency of about 10^7 cycles per second, deuterons of 32 M.e.v. energy and α-particles of about half that energy have been obtained by means of this method. High-energy neutrons, of course, cannot be obtained directly from the cyclotron, but must be produced from an ordinary disintegration reaction with the use of high-speed charged particles. Thus a particularly intense stream of neutrons is given by lithium, beryllium, boron, etc., when bombarded with accelerated deutrons. Recently a similar device has been used to obtain greatly accelerated electrons.

Examples of nuclear disintegration reactions are given in the following list.:

Type of Reaction.	Example.
(n, α)	$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{11}_{5}B + ^{4}_{2}He$
,,	$^{6}_{3}Li + ^{1}_{0}n \longrightarrow ^{4}_{2}He + ^{3}_{1}T \text{ (or } ^{3}_{1}H)$
,,	$^{10}_{5}B + ^{1}_{0}n \longrightarrow 2^{4}_{2}He + ^{3}_{1}T$
(p, α)	$^{6}_{3}Li + ^{1}_{1}H \longrightarrow ^{4}_{2}He + ^{3}_{2}He$
,,	$^{9}_{4}Be + ^{1}_{1}H \longrightarrow ^{4}_{2}He + ^{6}_{3}Li$
,,	$^{19}_{9}F + ^{1}_{1}H \longrightarrow ^{4}_{2}He + ^{16}_{8}O$
,,	$^{11}_{5}B + ^{1}_{1}H \longrightarrow 3^{4}_{2}He$

Type of Reaction.	Example.
(p, α)	$^{14}_{7}N + {}^{1}_{1}H \longrightarrow {}^{4}_{2}He + {}^{11}_{6}C$
	$^{9}_{4}Be + {}^{1}_{1}H \longrightarrow {}^{10}_{5}B + \gamma$
(d, α)	$^{6}_{3}Li + {}^{2}_{1}D \longrightarrow 2{}^{4}_{2}He$
	(Cf. $^{9}_{4}Be$, $^{10}_{5}B$, $^{11}_{5}B$, $^{12}_{6}C$, $^{14}_{7}N$, etc.)
(d, p)	$^{7}_{3}Li + {}^{2}_{1}D \longrightarrow {}^{8}_{3}Li + {}^{1}_{1}H$
(d, n)	$^{9}_{4}Be + {}^{2}_{1}D \longrightarrow {}^{11}_{5}B + {}^{1}_{0}n + \gamma$
	(Cf. $^{11}_{5}B$, $^{19}_{9}F$, $^{23}_{11}Na$, etc.).

The same isotope may disintegrate in different ways;

$$^{2}_{1}D + {}^{27}_{13}Al \longrightarrow \begin{cases} {}^{25}_{12}Mg + {}^{4}_{2}He \\ {}^{28}_{13}Al + {}^{1}_{1}H \\ {}^{28}_{14}Si + {}^{1}_{0}n \end{cases}$$

$$^{2}_{1}D + {}^{11}_{5}B \longrightarrow \begin{cases} {}^{9}_{4}Be + {}^{4}_{2}He \\ {}^{12}_{6}C + {}^{1}_{0}n + \gamma \\ 3{}^{4}_{2}He + {}^{1}_{0}n \\ {}^{12}_{5}B + {}^{1}_{1}H \end{cases}$$

$$^{2}_{1}D + {}^{2}_{1}D \longrightarrow \begin{cases} {}^{3}_{1}T + {}^{1}_{1}H \text{ (ND}_4\text{Cl on target)} \\ {}^{3}_{2}He + {}^{1}_{0}n \text{ (D}_3\text{PO}_4 \text{ on target).} \end{cases}$$
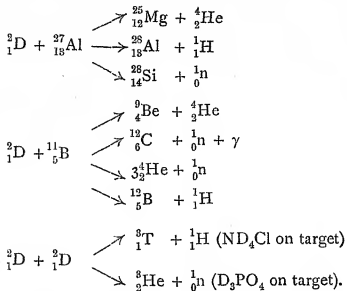
Artificial Radioactivity.—In 1934, Curie and Joliot first reported the artificial production of radioactivity in light elements. A piece of aluminium foil, when bombarded with α-particles, underwent the following reactions :—

$$^{27}_{13}Al + {}^{4}_{2}He \longrightarrow {}^{30}_{14}Si + {}^{1}_{1}H \text{ (95 \%)}$$
$$^{27}_{13}Al + {}^{4}_{2}He \longrightarrow {}^{30}_{15}P + {}^{1}_{0}n \text{ (5 \%).}$$
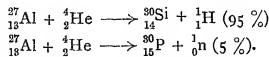
The phosphorus isotope formed by the smaller fraction of the aluminium atoms is metastable and disintegrates with the emission of a new particle, the *positron* or *positive electron*.

$$^{30}_{15}P \xrightarrow{t_{\frac{1}{2}}=3\cdot2 \text{ min.}} {}^{30}_{14}Si + {}^{0}_{1}e.$$
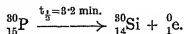
This new radiation, which had previously been detected in the cosmic rays, was emitted in increasing amount during irradiation till a constant maximum value was reached ; when irradiation was discontinued, the activity diminished exponentially with time. The radioactive substance was shown to be phosphorus by the following chemical tests : (a) the aluminium was dissolved in hydrochloric acid, the gas evolved (PH_3)

carried the activity; (b) the aluminium was dissolved in nitric and hydrochloric acids, and zirconium and sodium phosphate added to the solution; the activity accompanied the precipitated zirconium phosphate.

A great number of radioactive isotopes of lighter elements have now been reported; they are all β-active, emitting either positrons or electrons. The following table summarises a few of the reactions involved in the production of these isotopes.

Bombarding Particles.	Target.	Type of Reaction.	Metastable Product.	Disintegration Products.	Half-life Period.
α	^{10}B	(α, n)	^{13}N	$^{13}C + {}_{1}^{0}e$	11 min.
α	^{7}Li	(α, p)	^{10}Be	$^{10}B + {}_{-1}^{0}e$	
α	^{24}Mg	(α, n)	^{27}Si	$^{27}Al + {}_{1}^{0}e$	
α	^{25}Mg	(α, p)	^{28}Al	$^{28}Si + {}_{-1}^{0}e$	
α	^{26}Mg	(α, p)	^{29}Al	$^{29}Si + {}_{-1}^{0}e$	
p	^{12}C	(p, γ)	^{13}N	$^{13}C + {}_{1}^{0}e$	11 min.
d	^{10}B	(d, n)	^{11}C	$^{11}B + {}_{1}^{0}e$	20 min
d	^{14}N	(d, n)	^{15}O	$^{15}N + {}_{1}^{0}e$	126 sec.
d	^{16}O	(d, n)	^{17}F	$^{17}O + {}_{1}^{0}e$	1·16 min.
d	^{23}Na	(d, p)	^{24}Na	$^{24}Mg + {}_{-1}^{0}e$	15·5 hr.
n	^{27}Al	(n, α)	^{24}Na	$^{24}Mg + {}_{-1}^{0}e$	15·5 hr.
n	^{27}Al	(n, p)	^{27}Mg	$^{27}Al + {}_{-1}^{0}e$	10 min.
n	^{27}Al	(n, γ)	^{28}Al	$^{28}Si + {}_{-1}^{0}e$	2·3 min.

In practically all the above examples, the active isotope is produced by a reaction of smaller probability than the main reaction; often, the products of decay are identical with the products of the main reaction. The following general rules may be noted. (a) If the main reaction is (α, p), then a branch reaction (α, n) gives a metastable isotope of the bombarded element. (b) A (d, n) reaction may give a stable isotope of the next highest element; if a (d, p) reaction also occurs, it gives a metastable isotope of the element bombarded, which passes into the next highest element with the emission of β-rays. (c) If a (d, p) change leads to a stable species, then a branching (d, n) change will often give a metastable isotope, which, by losing a positron, passes into a stable isotope of the element bombarded.

In neutron bombardment there are two useful sources of neutrons; beryllium mixed with natural α-rayers, and beryllium subjected to high-speed α-particles. The velocity of the neutron may be adjusted to practically any value down to that corresponding to thermal energy by making use of the so-called water effect. When neutrons pass

through a substance rich in hydrogen, such as water, paraffin wax, etc., their energy is reduced by collision with the hydrogen atoms. If these "slow neutrons" are employed as bombarding particles, an interesting series of reactions involving neutron capture may be investigated. The nucleus which captures a neutron usually becomes β-active.

Transuranic Elements.—The most interesting development in this field has been in connection with the bombardment of the heaviest nuclei, such as uranium and thorium, which elements give rise to β-active products. The capture of a neutron does not alter the atomic number of the element bombarded, so that if the product from uranium is β-active, the recoil atom in this disintegration would be expected to be element No. 93, or Eka-rhenium. More careful observation showed that this β-activity was very complex, and about thirteen different half-life periods had been recognised by early 1940; some of these were allotted to the various "transuranic elements" in accordance with the following scheme :

$$_{92}^{238}\text{U} + {}_{0}^{1}\text{n} \longrightarrow {}_{92}^{239}\text{U} \xrightarrow[\text{10 sec.}]{\beta} {}_{93}^{239}\text{Eka-Re} \xrightarrow[\text{2·2 min.}]{\beta} {}_{94}^{239}\text{Eka-Os}$$

$$\Big\downarrow \beta \ \text{59 min.}$$

$$_{97}^{239}\text{Eka-Au} \xleftarrow{\beta} {}_{96}^{239}\text{Eka-Pt} \xleftarrow[\text{66 hr.}]{\beta} {}_{95}^{239}\text{Eka-Ir}$$
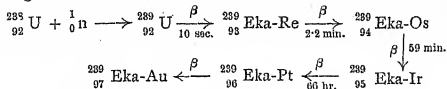
The properties of these very heavy elements were deduced from their position in the periodic system, and in several cases a considerable amount of chemical evidence was obtained to substantiate their existence. In general, there were difficulties in fitting the properties into the proper place in the table, but these transuranic elements certainly did not exhibit the properties of elements between Bi and U, and it was not thought that nuclei lighter than Bi would be formed. Curie and Savitch (1938) had, however, identified active bodies from uranium with rare earth-like properties, and Hahn and Strassman also found isotopes of barium and suggested that these might result from the cleavage of the uranium nucleus into two more or less equal parts ;

$$_{92}\text{U} \longrightarrow {}_{56}\text{Ba} + {}_{36}\text{Kr}$$
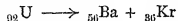
O. R. Fritsch put forward the view that the capture of a neutron by such a heavy nucleus as uranium might cause sufficient deformation to bring about a cleavage, the resulting fragments being then so violently separated by the electrical forces that recombination was impossible. Heavy fission fragments were later detected by physical means, such as their ionising properties, and their radioactivity was demonstrated after collection on a charged plate.

These discoveries have disposed of the majority of the so-called transuranic elements, since most of the half-life periods once attributed to them have now been identified with one or other fission fragment. These elements have, in fact, been identified as lanthanum, iodine tellurium, barium and the rare gases ; there remains still, however, the

60-day activity of the neutron-bombarded uranium, which may be due to Eka-rhenium.[1]

Substantially similar results have been obtained with thorium, and indeed some of the fission fragments from both these heavy elements are identical.

Calculations indicate that an energy of about 200 M.e.v. is released when a neutron causes the fission of a uranium nucleus. It is known that a twenty-fifth of this amount of energy would suffice for the liberation of a neutron from the uranium nucleus, so that the observation that about 2·3 neutrons are expelled at each fission causes no surprise. The possibility presents itself of a nuclear chain reaction, in which one neutron is captured by a uranium nucleus which is immediately cloven and in the process about two more neutrons are liberated. These should be capable of setting up further fission reactions, and so on, so that a chain reaction would occur in which there was a tremendous release of energy. The possibility of realising this extremely energetic reaction is much more remote than it appears at first sight; in the first place, the number of bombarding neutrons which are captured by the uranium is a small fraction of the total number; again, the mean free path of the neutrons in a mass of uranium is quite large; further, many of the neutrons would undergo resonance capture without causing fission. A discussion of this matter will be found in the Annual Reports of the Chemical Society for 1940.

Radioactive bodies, like stable isotopes, have been used as tagged atoms in many investigations of reaction mechanisms and in other problems. Their employment is conditioned by their half-life period and by the ease with which their activity can be detected. The student is referred to monographs on the subject.

Nuclear Isomerism.—There are now many examples of nuclei having the same atomic numbers and the same atomic weights behaving differently as regards their radioactivity. This phenomenon of nuclear isomerism is believed to result from the existence of different energy states in nuclei. In the upper, or excited state, a nucleus may lose energy either by direct radiation of α-rays, or by transfer to extranuclear electrons; the latter process is called internal conversion. Isomerism of this type may be observed only if the energies of the two states differ very slightly, while their rotational momenta are widely different, since under these conditions a transition would be highly forbidden.

[1] Macmillan and Abelson, *Phys. Rev.*, 1940, **57**, 1185.

MODIFICATIONS OF THE ELEMENTS—(A) GENERAL

Allotropy—Monotropy and enantiotropy—Dynamic allotropy—
The colloidal state—Colloidal solutions of elements

Allotropy

SUBSTANCES which are built up of atoms of the same kind often have very different properties. The property which these substances, both elements and compounds, possess of existing in different modifications is known as allotropy. There are two causes of this allotropy. In the first place, the atoms in the molecules may be differently arranged, thus producing a different molecular structure. Examples of this are seen in the modifications of carbon—diamond and graphite—in the rhombic and monoclinic forms of sulphur, or in the white and grey modifications of tin. All these variations, which are due to differences in the arrangement of the atoms in the molecules, are known as *primary modifications*, because they are dependent on the arrangement of the primary constituents.

Secondary modifications are those in which the arrangement of the larger groups of molecules differs enough to cause a substantial divergence in the properties of the element. The smaller particles of the different secondary modifications in the same element may be identical, not only those in the molecules but also in the smaller groups of molecules from which the large ones are formed. Examples of secondary modifications are seen in the different colloidal forms of the same substance, or the various structures of the metals deposited electrolytically (compact, smooth, polished, crystalline or powdery). In these the similar separate products of deposition have combined in different ways to form larger groups. Chemical reactions and physical properties are more dissimilar in the primary than in the secondary modifications.

Primary Modifications

Relation of the Forms to one another.—The stability of structures built up of an equal number of atoms is variable, being dependent on their arrangment. The internal forces which are liable to cause the atoms to alter their position can be resisted, but without the application of some external energy their effects cannot be reversed. Moreover,

the atoms cannot undergo any change involving an increase of energy unless this transformation is caused by an external force. If, therefore, a change takes place in an atomic system without a corresponding addition of external energy, the change itself must liberate energy.

Thus the second law of thermodynamics is applicable; and if, with an addition of energy from without, a change took place in a system of atoms whereby heat was produced, such a phenomenon would be contrary to this law. Thus, if a modification is effected in a chemical system by an external force, the change will take place in accordance with the nature of the force, and in such a way that its power will, if possible, be lessened. Hence pressure results in a decrease of volume; expansion, in order to regain the necessary energy, results in a lowering of temperature, and so on. A substance tends to react to a force in such a way as to effect a change which will act against the force and never so as to increase it. In other words, the system seeks to escape the force by weakening it. This is known as *Le Chatelier's Principle.*

A consideration of the range of existence and conditions of transformation of allotropic forms gives many examples of the application of this law. Spontaneous transition from one modification to another occurs only if the potential energy of the system is thereby decreased; the most stable modification possesses the least energy. The transition to a form of higher potential energy can be accomplished, provided that the addition of energy from without is greater, or at any rate equal to, the amount consumed in the transformation.

The liberation of energy can take place in different ways. In a chemical process it always takes the form of heat, at any rate in part; that is, the resultant, more stable body is warmer than the original substance. If it is subsequently brought back to its original temperature, a corresponding withdrawal of energy will occur: this will have the result of decreasing the individual vibrations of the constituents of the substance, for these reflect wholly or partially the energy which it possesses. These vibrations in the molecule, on the other hand, cause them to be borne away from the general mass by evaporation—thus in the change to a more stable form the vapour pressure is *lowered* and the power of reaction is reduced; for instance, in a reaction producing heat, for example combustion, less heat is produced by the stable form than by the labile, because part of the heat of the reaction must first make up that which escaped during the transformation from the labile to the stable form. The total heat effect is independent of the course taken by the reaction, *e.g.*:

Labile elem. + O = Oxide + m Cal.
Stable elem. = Labile elem. − n Cal.
Stable elem. + O = Oxide + $(m - n)$ Cal.

It is thus seen that a chemical substance can be transformed into a modified form without the addition of external energy, if this change causes a liberation of heat and a decrease of vapour pressure. This is true not only of primary, but also of such secondary modifications as develop into more stable and less reactive structures by a decrease in surface. Such transformations can take place by themselves, but they usually require a certain impulse. When this is lacking it is possible for labile bodies to remain for a long time without change; for example, many metals exist in labile forms at normal temperatures, and their change to a stable form is so difficult to achieve that it is only recently that the latter forms have been discovered.

Allotropy.—Elements which form crystals built up of polyatomic particles show the greater tendency towards allotropic modification, as it can take the form of a closer packing of the atoms, as in rhombic and monoclinic sulphur, both of which consist of groups of octatomic molecules. Another form of allotropy is found in the decomposition of the groups of atoms into smaller particles (depolymerisation), as, for example, the different forms of oxygen, O_2 and O_3, and also in phosphorus, arsenic, selenium, etc. Monatomic elements, *i.e.* the rare gases and the pure metals, are less liable to these changes, although they are not impossible in the solid state, as a crystal is itself a polyatomic molecule (see p. 18), the component parts of which can be put together in various ways. Different modifications are, however, particularly common among the polyatomic metalloids in Groups IV, V and VI, and in those metals whose crystalline structure shows that they approximate to non-metals. Among the non-metals the existence of allotropy has been longer known than in the metals, because it is much more noticeable, as in the allotropic modifications of non-metals there is a great difference in physical and chemical properties (graphite, diamond; oxygen, ozone; red and white phosphorus, etc.).

It has been found that the transition from one modification to another can be effected in three different ways: (1) B can be transformed into A by the same means whereby A becomes B; *e.g.* the process may be carried out by a change of temperature (change of pressure has a similar effect), in which the one form is stable below a certain temperature (the transition point), while above this point the other form is stable. An example of this kind of transformation is seen in rhombic and monoclinic sulphur. It is known as *enantiotropy.* (2) When at all temperatures the transformation proceeds from one form to the other, but never in a reverse direction, the modification is known as *monotropic.* Examples of the latter are found in the forms of oxygen, in which O_3 can be transformed into O_2, but not O_2 into O_3. This transformation, which cannot be effected spontaneously, may be brought about through an intermediate form which must, however, be enantiotropic to both the others. An example of this is

seen in the forms of oxygen where the free atoms can combine to form either O_2 or O_3, and can be formed either from O_3 or from O_2. In other instances a substance is monotropic in the solid state, but enantiotropic when fused, and the unstable solid form is arrived at indirectly by melting.

FIG. 23.

(3) Finally, a third kind of allotropy is *dynamic*, in which both forms always exist side by side, in a stable condition. The quantitative relationship of the forms—for example, Elem.$_n \rightleftharpoons n$Elem. — is dependent on the temperature, so that at high or low temperatures the equilibrium can take up a position in which practically only one form is present. In all probability the allotropy of red phosphorus is dynamic, as is also that of many metals; in fact, this form of allotropy occurs more frequently than has hitherto been supposed.
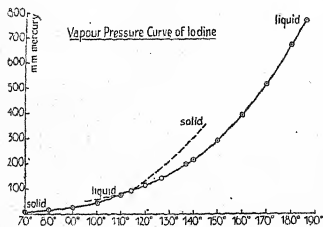
Allotropy and Vapour Pressure.—It is not difficult to ascertain whether certain modifications are monotropic or enantiotropic if their respective vapour pressure and temperature curves are known. Fig. 23 represents this curve for iodine. Atmospheric pressure is reached at 186°. The diagram consists of two curves, the lower of which represents the vapour pressure of solid and the upper of liquid iodine— the point at which they intersect (114·1°) is the melting point[1] of iodine; here the vapour pressure of the solid and liquid forms is equal; therefore at this point both forms are equally stable. The dotted lines represent the partly hypothetical continuations of the two curves; the continuation of the vapour pressure curve of liquid iodine, represented by the broken line towards the left at the bottom of the diagram, shows the (determined) pressure curve of under-cooled liquid iodine, while the dotted line continued to the right (at the top) represents the (unverifiable) curve of superheated solid iodine: the stable form is always represented by the lowest curve. Thus under-cooled liquid iodine can change spontaneously into the stable solid state, and similarly, superheated solid iodine changes into the stable liquid form. There is so far no reliable indication that solid substances can be superheated above their melting points, but they are stable above their transformation points, if another solid form exists which possesses a higher melting point.

[1] In a wide sense the transformations   solid $\rightleftharpoons$ liquid   are enantiotropic.
$\rightleftharpoons$
gas

Enantiotropy.—These relations may now be discussed for an element which occurs in the liquid state, as well as in several solid forms; the rhombic, monoclinic and liquid forms of sulphur are a good example.

The figure (24) shows a simplified [1] temperature-pressure diagram of three forms of sulphur. The lower portions of the curve shown by the continuous lines represent the stable forms. Below 95·6° rhombic sulphur is the most stable; between 95·6° and 120° the monoclinic form, and, above 120°, liquid sulphur. The labile states of the three forms are represented by the dotted lines, the superheated forms by the curves which are continued upwards, and the under-cooled by the curves extended downwards to the left. Two forms are in equilibrium at the intersection
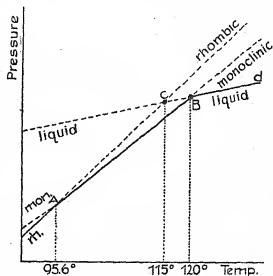
FIG. 24.—Equilibrium diagram of sulphur.

points of the two curves — at A, rhombic and monoclinic sulphur; at B, monoclinic and liquid sulphur; and at C, (superheated) rhombic and the under-cooled liquid. If the liquid form, originally in the condition represented by *d*, is gradually cooled, it is transformed into monoclinic at B, but not into rhombic sulphur, because the vapour-pressure curve of the latter is higher than that of either the liquid or the rhombic form. The separation of monoclinic sulphur may be avoided if the temperature is sufficiently rapidly lowered, and by this means liquid sulphur in an under-cooled state may be obtained. If this crystallises between B and C the product will always be monoclinic sulphur, because its vapour pressure curve is the lower. Below C, however, rhombic sulphur may be deposited, for, although the latter has a higher vapour pressure than monoclinic, it is nevertheless lower than that of liquid sulphur; but the rhombic shows here a strong tendency to change into the monoclinic form. If the temperature of the under-cooled melted mass is below 95·6° monoclinic sulphur is at most only temporarily formed, since the rhombic is then the more stable form. At 95·6° both forms possess the same vapour pressure, and are therefore equally stable. A rise of temperature causes a mixture of both forms to change into monoclinic sulphur, but if the temperature is lowered the rhombic form always appears. The melting points, *i.e.* the transition points of the two solid and the liquid forms of sulphur, are higher (115° and 120°).

The fundamental condition of enantiotropy is that the transition

[1] In reality the conditions are more complicated, *cf.* p. 124. A good example of enantiotropy in compounds may be seen in *a* and *β* quartz (p. 813).

points of the two solid forms occur at a temperature which is *below* their melting points.

Monotropy.—The conditions of monotropy follow from the above considerations. This state obtains when the point at which the two solid forms would be transformed into one another lies *above* the temperatures at which they change into a different state of aggregation. The resultant conditions are represented in the accompanying diagram.
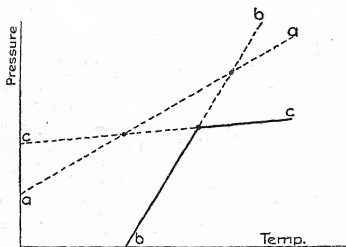
FIG. 25.—General diagram of a monotropic change.

The solid forms are indicated by a and b, the liquid by c. Each vapour-pressure curve intersects that of the liquid form; the points of intersection therefore represent their melting points. But the intersection point of aa and bb lies above curve c—that is, above the respective melting points of the two forms, and superheated solids cannot exist when the liquid form is more stable. If, however, the melted mass is under-cooled, it can crystallise into the lower form at a; but this in its turn is labile, and can be transformed into b. The same result is obtained if the third form is represented by the vapour instead of the melted mass. It is possible to separate off the labile form from under-cooled vapour. Very often b is a polymer of a, and depolymerisation takes place on the vaporisation of b, but condensation is not always immediately succeeded by repolymerisation. The belief has long been held that phosphorus is monotropic, because, although the white variety gradually changes to violet without being vaporised, it is not possible to transform the violet phosphorus into white without distilling it (*cf.* p. 135).

Dynamic Allotropy.—This form of allotropy obtains when two forms existing side by side remain stable over a wide interval without a third form as intermediate stage. The relative quantities are dependent on temperature and pressure. Examples are found in both liquid and gaseous systems, *e.g.*:

$$S_8 \rightleftharpoons 2S_4, \quad As_4 \rightleftharpoons 2As_2, \quad I_2 \rightleftharpoons 2I, \quad H_2 \rightleftharpoons 2H.$$

These transformations are distinguished from enantiotropy and monotropy by having no definite transition point, for both forms exist together over a wide range. The existence of the mixtures is, however, restricted, for at the same pressure and temperature the quantity of the components in equilibrium cannot vary but is definitely

fixed, and the relative quantities, though constant for a given temperature and pressure, must alter with a change in either. Thus dynamic allotropy occurs and can only occur when the entire system is homogeneous—in other words, when the system is either a gas or a homogeneous liquid, or if it forms a homogeneous solid solution.

The position of the equilibrium in this form of allotropy is governed by the law of mass action; a good example is seen in $I_2 \rightleftharpoons 2I$. At about $1110°$, and under atmospheric pressure, 50 per cent. of the molecules are split up into atoms. If the iodine vapour in equilibrium at $1100°$ is compressed, the increase in pressure, in accordance with Le Chatelier's Principle, will favour the reaction which proceeds with diminution in volume, i.e. the formation of I_2 molecules. If, on the other hand, the vapour is heated while the pressure remains the same, in accordance with the same Principle, increase in temperature will favour the reaction which proceeds with absorption of heat, i.e. the formation of I.

If, as in iodine vapour, the equilibrium immediately follows a change of temperature, this would not formerly have been regarded as allotropy. But in other cases, more especially in solutions or in liquids (modifications of melted sulphur, cf. p. 124) and particularly in solids (so-called red phosphorus, which is really a combination of white with metallic phosphorus, cf. p. 135), the substances take some time to reach equilibrium, and hence the allotropy is at once recognisable. The liquid or solid forms which attain their equilibrium at higher temperatures may sometimes be kept for short or even for long periods at room temperature, and easily assume certain special "modifications," while being in reality merely combinations of two already recognised modifications.

This conception of allotropy can be extended so as to include both the polymerisation and depolymerisation of elements. Depolymerisation may be observed in all polyatomic molecules, either at a sufficiently high temperature or under the influence of electric discharges, after which the molecule returns to its original state by polymerising or producing yet another combination of atoms, which will then possess a different stability. An example is found in oxygen:

$$O_2 \rightleftharpoons O \longrightarrow O_3 \longrightarrow O_2 + O.$$
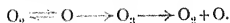
The transformation $O_2 \rightleftharpoons O_3$ differs from the allotropy previously discussed—in that it does not take place directly, but through the medium of free oxygen atoms. Thus an allotropic transformation is produced by two separate reactions, a knowledge of which makes it possible to form some idea of the method of formation of the molecules. The first reaction consists of the formation of free atoms of oxygen from O_2; this can only take place with the addition of energy (heat); on the other hand, the oxygen atoms combine into molecules with liberation of energy (heat). According to Le Chatelier's Law, as a certain amount of heat is consumed in the formation of free atoms, a rise in temperature facilitates the process.

In the separation of O from O_3 the conditions are reversed—this reaction is exothermic, and heat is given off during this process. The cooler the surroundings the more easily will this take place, and hence the higher the temperature the more stable the ozone. The stability of endothermic substances increases with rise of temperature, while exothermic substances are more stable at lower temperatures. Care must be taken in the application of this rule, for not only does the thermal effect of the reaction vary with the temperature, but under certain conditions it may be completely reversed; moreover, there are other factors, dealt with in text-books on physics, which prevent the invariable application of this rule.

In the present example the formation of ozone is facilitated by passing the oxygen through a region of high temperature, because it assists the production of the essential atomic oxygen. At high temperatures, both O_2 and O_3 produce free atoms of oxygen which can reunite into O_2; if it is desired to retain a large quantity of O_3 it is necessary to render it feebly reactive, so as to retard decomposition. This is possible if the ozone is very rapidly transferred from the region of high temperature to one of low temperature; the equilibrium is then more unfavourable to the existence of the ozone, but the speed of the transformation to the stable form is diminished. Hence ozone which has been produced by heat must be removed as rapidly as possible from the temperature at which the reversible action $O_2 \rightleftharpoons O \rightleftharpoons O_3$ shows a marked movement to the left, for although not actually on the left-hand side, the state of equilibrium is very rapidly attained. At very high temperatures the decomposition of the ozone molecules into atoms of O is also increased, hence a diagram showing temperature and quantity of the three forms of oxygen has the form shown in Fig. 26.
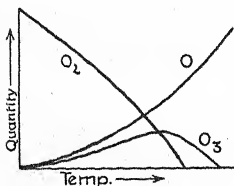
FIG. 26.—The formation of ozone.

It must here be noted that the allotropy of oxygen is not dependent on one equilibrium, but on two concurrent or superimposed reactions; as a result, none of the three forms has any definite transition point, but they can exist simultaneously over a wide range, though in quantities varying according to temperature, pressure and period of reactivity.[1] (See further, p. 119.)

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[1] The formation of ozone at a low temperature can also be brought into relationship with the following law: in a substance existing in three forms, a, b and c, in which a possesses the most and c the least energy, a can be transformed into b as well as into c by giving up energy. According to a general law (Ostwald) this always occurs in stages, and the labile b is formed first and then the stable c; a is not transformed directly into c. Of course, the time of existence of b is very short.

Colloidal Forms of the Elements

The secondary modifications due to the formation of crystals from the primary particles, as in graphite, phosphorus, etc., have already been discussed (p. 21). But the structure of the primary forms need not be crystalline; examples frequently occur among the extensive groups of colloidal substances in which the position of the atoms shows no conformity to any law. This amorphous condition is not, however, an essential of the colloidal state; on the contrary, colloids are known to exist which unquestionably possess a crystalline structure, such as certain forms of albumen and crystalline colloidal metals such as silver or gold.

A complete exposition of colloid chemistry, which in this century has developed into an altogether separate branch of learning, lies outside the scope of this book. The phenomena of colloid chemistry are, however, of such importance that the properties and behaviour of a great many inorganic substances cannot be understood without some knowledge of this science.

The Colloidal State.—The outstanding feature of the colloidal condition is that the particles of one form of matter are finely divided and separated by a continuous medium of different composition. The term is extended to include homogeneous solids which can be brought to this condition by treatment with a dispersion medium (peptisation). The state of the particles in an ordinary crystalloidal solution or in a gas is also roughly covered by this definition, but there are other important conditions which obtain in the colloidal state. In the latter the particles are practically always composed of a considerable number of molecules, while in ordinary solutions the molecules or ions exist as such or are only slightly polymerised; further, the colloidal particles can be caused to reunite to form precipitates without visible change in the position of the solvent (coagulation). The most characteristic form of the colloidal state is the colloidal solution, and solids are only termed colloidal when they can form, or are formed from, a colloidal solution. The existence of the two phases is essential for the colloidal state, and the most typical examples are the solid-liquid systems incorrectly referred to as colloidal solutions.

Colloidal solutions lie as an intermediate stage between true solutions and coarse suspensions. The particles in them are electrically charged, although they are much larger than the ions of solutions of electrolytes. The colloidal character is determined in the first place by the size of the particles, and secondly by their electric charge.

Owing to their large size compared with molecules, the colloidal particles are unable to pass through small pores, and it is on this property that the original distinction between colloids and crystalloids was based. Graham, the founder of the science of colloid chemistry, demonstrated that colloids were unable to diffuse through membranes

with fine pores (dialysis) or through jellies. Naturally, the possibility of diffusion is dependent on the sizes of the pores of the membrane and that of the colloidal particles. In typical colloidal solutions the diameter of a particle lies between $\frac{1}{100000}$ and $\frac{1}{1000}$ mm.; that of the particles in a crystalloid solution is a thousand times smaller. There are wide variations in particle size in different types of colloidal solutions. Emulsions contain particles of diameter $0.5 - 5.0 \, \mu$; hydrophobic sols have particles with diameters ranging from a few $\mu\mu$ to 100 $\mu\mu$. The colloidal particles do not settle appreciably under the influence of gravity, so that they do not form a sediment like ordinary suspensions ; they are, however, brought down by centrifuging. The particles move in the colloidal solution in all directions like the molecules of a gas, but seldom come into actual contact owing to their charges being all of the same sign. The consequent repulsion is but a small factor compared with the kinetic vibrations. Particles of diameter about $\frac{1}{10000}$ mm. are visible in the ultramicroscope, and their irregular movements can then be seen (*Brownian Movement*). This movement is due to the thermal energy of the particles and remains unaffected by the action of external influences such as light or the general motion of the liquid. The smaller the particles the more vigorous the Brownian movement, which continues as long as the solution exists, and has been observed to go on for years. If the particles coalesce so that their size is increased to $\frac{1}{1000}$ mm., the movement almost ceases, and this represents the limit of the colloidal solution, which then begins to coagulate, sediment or gelatinise, or, if it is a suspension of liquid droplets (emulsion), the disperse phase separates as oily drops.

The particles in a *coarse* colloidal solution settle slowly under the influence of gravity, and hence there are more particles in a given layer nearer the bottom of the vessel than in the upper layers. The laws of the kinetic theory hold for these solutions, and Avogadro's constant (N) has been calculated from the distribution of the particles.

In true solutions the particles behave as if the solute were in the gaseous state in the volume occupied by the solution, and the same idea holds good for colloidal solutions. The phenomena of diffusion and of osmosis are similar, but in colloidal solutions the osmotic pressure is very low, owing to the large size and comparatively small number of the particles.

The large particles in a colloidal solution may be single molecules of great size, as in hæmoglobin, but are more frequently aggregates of molecules, as in the colloidal elements. The size of the particles can vary a good deal, even in the same solution. Siedentopf and Zsigmondy called particles too small to be seen under the microscope ultramicrons, those visible with the ultramicroscope, submicrons ; while some, too small to be visible even with this instrument, are called amicrons. The size of the particles can be found most directly by

ascertaining the number in a given volume and the total weight of the disperse phase in some multiple of this volume.

The electric charge on the particles prevents them from coalescing under ordinary conditions. It also causes them to move in an electric field in just the same way as ions. If the charge is removed the particles usually coagulate and the sol (*i.e.* the colloidal solution) gives a gel (a product of coagulation). The coagulation due to the removal of the electric charge may be brought about directly by the electric current, when the particles form flakes at the electrodes, or it can be effected by the addition of electrolytes (acids, bases or salts); the ultramicrons adsorb oppositely charged ions and thereby become discharged. Although each particle may carry several unit charges, the total number on a particle is less than there would be if each of its constituents functioned as an ion. Thus colloidal solutions do not appear to conform to Faraday's Law : To liberate a gram-equivalent of an ion from a solution requires 96,500 coulombs, but this quantity of electricity is sufficient to discharge a much larger quantity of material from a sol—up to 6 or 8 g.-eq. This is due to the fact that the particles in the sol are complex and made up of a large number of primary particles, so that the electro-chemical equivalent of the mass cannot be predicted, although it is certainly greater than the sum of those of the primary particles of which it is built up. When ultramicrons carry several charges they can be partially discharged by the addition of small quantities of electrolytes; their stability is greatly diminished, and they coagulate even when subjected to a potential 0·03 volt below that required to bring the sol to the isoelectric point (Hardy). The latter is readily determined by the cessation of movement in the electric field; the Brownian movement, naturally, still continues even under these conditions, as it depends on the smallness of the particles and not on their charge.

When colloidal solutions are precipitated by electrolytes, polyvalent ions are naturally more effective than univalent ions. The precipitation of negative colloids depends on the cation present, that of positive particles on the anion. For example, the following quantities of electrolytes precipitated the same quantity of (negative) arsenic sulphide sol[1] :

NaCl	CaCl$_2$	AlCl$_3$
51·0	0·65	0·09 millimols.

The valency of the ion, however, is not the only factor which affects the precipitation, as the ions are adsorbed selectively. When colloidal solutions containing particles of opposite charge are mixed, mutual precipitation occurs.

The origin of the electric charge on the particles is still a matter of controversy, but at least two factors operate to cause it. There is always a difference of potential at the surface of contact of two phases

[1] Picton and Linder, *J. Chem. Soc.*, 1895, 67, 63.

(Helmholtz's electrical double layer; see books on electro-chemistry), the substance of higher dielectric constant assuming the positive charge (Coehn). In the second place, the relatively enormous surface of the disperse phase causes great adsorption of the ions present in solution. The charges on the ions adsorbed are then transferred to the particles to which they cling, thus causing the large particle to become a kind of ion itself. Treatment of a solid mass with a solution containing suitable ions often causes it to go into colloidal solution. This process is known as peptisation, and very small quantities of electrolyte suffice for the peptisation of some solids. Thus, 1 g.-eq. of potassium hydroxide is enough to bring 200 g.-eq. of stannic acid into colloidal solution; the process seems to be somewhat as follows: the potash transforms an equivalent quantity of the stannic acid into stannate, K_2SnO_3. One of the aggregates of stannic acid $(H_2SnO_3)_n$ adsorbs a molecule of stannate giving a complex $(H_2SnO_3)_n$, SnO_3K_2, which dissociates into $[(H_2SnO_3)_nSnO_3]''$ and $2K'$. The precipitation of these colloids by heavy metal salts is thus easily explained, as the latter form insoluble salts, and it is found in practice that the precipitating ion is always removed by the colloidal particles. The osmotic pressure and conductivity of colloidal solutions is also to be explained on this basis. The ultramicrons by adsorbing ions acquire the properties of ions. The adsorption theory is not, however, essential for the explanation of the electric charge. According to the views of Kohlschütter and Frey[1] a gel particle may be considered as a giant molecule composed of a large number of ordinary molecules: if one of the latter is dissociated, one of its ions in combination with the rest of the great molecule gives a charged particle. The ion-adsorption theory, moreover, does not readily explain the existence of charged particles in non-ionising solvents.[2]

A gel can only be peptised when the small particles are present in the solid itself, a condition which is always fulfilled when it has a considerable content of water, the complete removal of which frequently makes it impossible to peptise the gel. The individual particles may each be enveloped in water and thus maintain their independence. There are numerous indications that in the coagulation of these peptisable gels the number of their individual particles remains the same; all that happens is that they are drawn closer together and have lost the power of repulsion. It is then possible to speak of solid colloids, although they are not strictly solid, nor are they colloidal until they have gone into solution. The particles repel one another when they become charged by the absorption of ions.

Colloids which can be transformed from the gel into the sol state and *vice versa* are termed reversible (or resoluble); those which cannot

[1] *Z. Elektrochem.*, 1918, **22**, 158.

[2] *Cf.* Hatschek and Thorne, *Proc. Roy. Soc.*, 1923, 103A, 276.

be thus transformed, irreversible (irresoluble). To the first class belong the peptisable colloids, although some of these need no peptising agents and, on the addition of a liquid medium, first of all swell (turgesce) and then lose their cohesion and form a solution (glue, gum, gelatin). When there is a strong affinity between the colloidal particles and the solvent, as with albumin, starch, silicic and stannic acids, the substances are described as *lyophile*. The pure colloidal metals belong to the irreversible class, and like most irreversible colloids have little affinity for the continuous medium, being therefore described as *lyophobe*. It is possible to make an irreversible colloid reversible, by mixing with it in solution a small quantity of a reversible colloid. This "*protective colloid*" appears to prevent the direct union of the particles of the irreversible colloid, almost as if it formed a skin over them, which completely shut them off from their surroundings. In this way the protected colloids acquire the reactions of the protective colloids. If gel formation takes place through the drying up of the colloid, this can be completely reversed if the protective skin is again caused to swell. Those substances, therefore, which swell in the medium are most suited to act as protective colloids, as they are much less liable to precipitation by electrolytes than those which do not swell. For example, in the case of a certain colloidal solution of gold, the protective power of various substances was as follows:

> Gelatin, 200; casein, 100; gum arabic, 5; sod. oleate, 2; dextrin, 1; starch, 0.04; $Si(OH)_4$ and $Sn(OH)_4$, 0.

On the other hand, addition of a very minute quantity of protective colloid results in the sensitisation of the lyophobe to electrolytes, *e.g.* a (negative) Fe_2O_3 sol may be tremendously sensitised to electrolytes by the addition of a little albumin. Rubber or soaps of multivalent metals protect lyophobe non-aqueous colloids.

The influence of a change of temperature on the stability is very variable. Heat frequently reduces the stability of the sol (coagulation of albumin by heat); it may also be highly conducive to the opposite process (heat is necessary to dissolve glue); frequently its influence is only slight (pure colloidal metals). On the other hand, the chief effect of freezing colloidal solutions is to cause separation of the gel, for the frozen solvent diminishes in quantity, and the solution becomes more concentrated; hence the distance between the particles is reduced; and this action has a similar effect to that produced by drying. Frozen gels are usually irreversible (metals) but may be reversible, especially in the presence of a protective colloid. In coagulation or peptisation the heat effect is very slight.

According to Freundlich, the liquid is the usual dispersion medium in both sols and gels, though in the gels the solid particles of the disperse phase are no longer free to move. The Brownian motion is

no longer seen in the gel, which usually has the properties of an elastic solid (a jelly), while the sol has the properties of a liquid. The change from sol to gel can be brought about by mechanical means as well as by those mentioned above. Thus a concentrated sol of Fe_2O_3 (about 5 per cent.) forms a pasty gel when a very little NaCl is added to it, but on shaking violently or on applying pressure, it is re-liquefied and then settles down to a gel form on standing for a time. Other sols can be induced to show this phenomenon (thixotropy) without the previous addition of electrolytes[1] (e.g. Al_2O_3, V_2O_5). Some thixotropic systems gelatinise very readily if moved in a regular circular fashion. This behaviour, known as *rheopexy*, is peculiar to systems having rod-shaped, elongated particles or plates.

The optical properties of colloidal solutions are very characteristic. If the ultramicrons are very small the light will be able to pass through the solution in the same way as it does through a solution of electrolytes; these solutions are "optically clear." If, on the other hand, the particles are large, a parallel beam of rays becomes visible when passing through the solution; it becomes linearly polarised (Tyndall's phenomenon). The cone, which is readily perceived, indicates at once the colloidal nature of the solution. A solution containing very fine particles is perfectly clear, but when the particles are coarse it becomes opalescent; moreover, it appears cloudy and almost opaque in reflected light, although when observed by the naked eye with the light shining through the solution, it appears quite clear. The colour also depends on whether the light is reflected from or passes through the solution. If the ultramicrons are colourless and very small, the solution will also be colourless; but if large, the opalescence of turbid liquids will be seen of various colours, even if the single particles are colourless. If, how-ever, they have a specific colour, this will be seen in reflected light; but when the light is passed through the solution it will appear to be of the complementary colour. Very often, however, and especially in the colloidal metals, the particular colour may be dependent on the size and structure of the single particles, as can be seen especially in those of gold and of silver (Carey Lea,[2] Wiegel[3]). The latter worker, by slowly adding hydrogen peroxide as reducing agent, obtained yellow, red, violet, blue, grey-green and grey as colours by transmitted light, and blue, green, olive-yellow, brownish red and finally the white sheen of compact silver by reflected light.

When superficially examined a colloidal substance almost always gives the impression of being amorphous; nevertheless it has long been recognised that crystalline substances are also able to form colloid solutions, and that a solution of crystallised albumin, for example, possesses an unquestionably colloidal character. Now, with the help

[1] Freundlich, "Thixotropy," 1935.   [2] *Amer. J. Sci.*, 1889, 37, 476.
[3] *Kolloid-Z.*, 1930, 51, 112.

of Röntgen ray analysis, Debye and Scherrer have been able to show that the atoms in the particles of a colloidal solution of silver are arranged in the same manner as in macroscopic silver crystal. The particles in sols of CuO, V_2O_5, Fe_2O_3, etc., are also crystalline. Similarly the structure of starch and other decided colloids closely resembles that of crystals; thus the view which was formerly held, that the primary particles of a colloid are quite without orientation, is disproved. The latter is lacking only when the primary particles are being built up into secondary particles. Thus the smallest particles have their orientation, but this is not always continued when they combine together. Sols of Al_2O_3, ThO_2, ZrO_2, S, and As_2S_3 do not show orientation of the primary particles unless they are aged (*cf.* p. 454).

Colloidal Elements.—Colloidal elements are of special interest, because their chemical relationships are the least complicated. A great many metals and some non-metals are known to exist in a colloidal form. An aqueous solution can naturally contain as "hydrosols" only those metals which are not chemically acted on by water; on the other hand, "organosols" of any metal in a colloid form can be prepared in suitable organic solvents.

There are two principal methods for producing colloidal metals; one consists in the disintegration of the compact metal, the other in the reduction of a compound of the metal in such a way as to hinder the formation of large particles. These are referred to as the dispersion and condensation methods respectively.

Dispersion can be accomplished by (1) vaporisation; (2) electrical pulverisation; (3) light energy. The third method is of little practical importance, but it is interesting to note that several metals (Ag, Cu, Pb, Sn, but not Au or Al) when covered with a solvent and under the influence of a mercury vapour lamp, liberate a visible quantity of colloidal particles into the solution in a few minutes. The method of vaporisation is of greater importance, but must of course be carried out at a higher temperature, and is particularly effective when dispersion media which can be liquefied by heat are employed; by this means the so-called pyrosols are obtained. For example, if zinc is introduced into melted zinc chloride, cadmium into cadmium chloride, or lead into lead chloride, these metals produce coloured fogs which spread through the molten mass; the intensity of the colour depends on the increase of vapour pressure when the temperature is raised. The production of these colloidal fogs in fused electrolytes hinders the electro-chemical separation of the metal from the melt (see p. 191). After cooling and solidification have taken place, the metal remains isolated in the compound in finely divided particles, often giving it the colour of the aqueous colloidal solution. A beautiful example of this is the ruby glass produced by heating copper, silver, and particularly gold, in melted lead or baryta glass. If the melted gold-ruby glass is

slowly cooled, it will be seen to be impregnated with innumerable ultramicrons of gold and will now possess the characteristic ruby colour peculiar to the aqueous colloidal solutions of gold. If, on the other hand, the cooling is carried out speedily, the solidified glass will be colourless, but if it is afterwards carefully re-heated, it will become red. Closely allied to these pyrosols is the coloured rock-salt obtained by treating heated sodium chloride with sodium vapour; also ultramarine, which may contain blue colloidal sulphur; and further, the solutions of sulphur in melted SO_3, and possibly also the blue solutions formed by the alkali metals in liquid ammonia, etc.

The pulverisation of the metals with the help of the electric arc makes it possible to obtain sols in cold solvents[1]; it is due to the local vaporisation of the metal. If noble metals are used as the electrodes and an arc with alternating current is formed between them under water, the water will become full of colloid particles in a very short time. Base metals can be made colloidal by the same method, if instead of water a solvent which will not react with them is employed. Thus it is even possible by using ether[2] to obtain colloidal solutions of alkali metals, the colours of which closely resemble those of the vapours of these metals. These solutions have the following colours:

Li	Na	K	Rb	Cs
Brown	Purple	Bluish green	Greenish blue	Bluish green.

Gases can also be employed as solvents, although the aerosols formed from metals are quite unstable and easily separate out. The deposits on the glass of incandescent electric lamps and radio valves are due to the precipitation of these aerosols. If a glow discharge is used to pulverise the metallic electrodes, the gas present has a remarkable effect on the form of the separated metal—the heavier the gas the more finely divided the metal; the lighter the gas the coarser the powder. The deposits obtained in argon are very different from those in oxygen.[3]

Reduction methods are the easiest and surest way of obtaining colloidal metals. Inorganic bodies may sometimes serve as reducing agents, e.g. hydrazine, hydrogen, phosphorus (in ethereal solution), carbon monoxide, but acetylene, and especially aldehydes (formaldehyde, sugars and essential oils) are often used. In the absence of protective colloids, only very weak metal sols can be obtained in this way, the metal content being generally less than 0·1 per cent., but when correctly prepared they can be preserved for years, and possess characteristic properties. Purity of the reagents is of the utmost importance in their preparation. If gold chloride and formaldehyde are boiled in dilute solution with a small amount of potassium

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[1] Bredig, Z. Elektrochem., 1898, 4, 514.

[2] Svedberg, Ber., 1905, 38, 3616; 1906, 39, 1705.

[3] Kohlschütter, Kolloid. Z., 1913, 12, 285.

carbonate, provided that the water is pure, a bright red solution of colloidal gold is obtained, which is very stable; this remains unchanged by heat; moreover, it can be somewhat concentrated by boiling.[1] The least trace of electrolytes will at once alter the gold solution, and by producing coarser particles will cause the solution to assume a blue-violet colour. Beautiful sols of gold are obtained if gold chloride is reduced with a solution of phosphorus in ether (Faraday). If small quantities of positive charges (acidification) are added to the red solutions they show a distinct change to blue, as is seen in indicators, the blue colour changing back into red when alkali is added. This phenomenon is due to a change in the structure of the particles. In the colloidal solutions of gold two kinds of ultramicrons can be distinguished; the first are green in reflected light, but the solution is red by transmitted light. It is possible that these are small compact homogeneous particles. The second consist of coagulated aggregations of the former particles which have formed larger flakes; their colour varies from yellow to brown and their suspension appears blue in transmitted light. Violet solutions contain both kinds of particles. The electrical charge of colloidal metals is almost invariably negative, hence a small number of positive $H^{.}$ ions produces a partial discharge which results in an increase in size of the particles; these enlarged molecules can then be partially peptised by negative OH' ions, which produce the opposite effect.

In the production of a colloidal solution of gold, the formation of small compact green ultramicrons starts when the number of growing particles of solid matter is very large; the conglomerated yellow-brown particles only begin to form when the number is small, but compensate for this by the rapid growth of the individual particles; hence the longer the reaction continues the larger can these brown particles become, and they produce a solution which appears blue in transmitted light. The speed of the reaction is, however, dependent on the nature of the reducing agent. Thus a certain solution of gold chloride gave the following numbers of particles in a volume of $1000 \mu^3$: with phosphorus, in a few minutes, 120,000; with formaldehyde, in two seconds, 5000; with hydroxylamine, in ten seconds, 5. A rise in temperature or concentration has the same effect; it hinders the formation of the nuclei but facilitates their growth. These two actions can also be influenced independently by external agents. For example, the formation of the blue coarsely granulated gold sols by means of formaldehyde, when a small quantity of electrolyte is present, is dependent on the electrolytes retarding the formation of fresh nuclei, so that the few present collect all the gold. One of the most powerful electrolytes with this effect is potassium ferricyanide; a quantity of only $7\cdot6 \times 10^{-8}$ millimols per litre will completely arrest the formation of fresh nuclei, but will have no effect on the growth of those which are already in existence or may be added later. Thus it is possible to regulate the size of the particles by putting a solution of ready-made nuclei into one in which there are no fresh nuclei. On the other hand, there are some substances which not only hinder but arrest the growth of the nuclei without checking their formation; to the latter class belong hydrogen sulphide, soaps, oils, etc.[2]

[1] Zsigmondy, *Ann.*, 1898, 310, 30; *Z. anal. Chem.*, 1901, 40, 711.
[2] Hiege, *Z. anorg. Chem.*, 1915, 91, 145.

The addition of protective colloids hinders or lessens the colour change of colloidal gold, for they prevent the particles from uniting and make their deposition difficult. Moreover, the ease of coagulation, which is related to the colour change, is likewise dependent on the structure of the electrolytes added, as well as on their valency (*cf.* p. 101). Even when they are amphoteric, large molecules are potent in causing precipitation and a sudden change of colour (*e.g.* albumins and alkaloids). Lastly, it should be noted that the colour of colloidal gold is also influenced by the orientation of the particles—it can be changed by pressure or expansion.

Colloidal gold can be taken up by certain substances in the same way as colouring matter—possibly by adsorption. Moreover, not only will other colloids—$Al(OH)_3$, stannic acid—become coloured in this way, but also finely powdered crystalloids ($CaCO_3$, $BaSO_4$).

The most permanent unprotected colloidal solutions of other metals are those of silver and platinum. The latter forms a brown liquid with up to 0·02 per cent. Pt, whether it is produced by electrical disintegration (Bredig) or by reducing with formaldehyde. Colloidal silver obtained by pulverisation frequently possesses, in addition to the brown colour, a distinctly grey tone—a mixed colour made up of innumerable nuances. No other sol shows more varied colours under the ultramicroscope; brilliant blue, red, purple, violet and shining minute white stars, all go to produce the grey colour of the solution. Sols of silver may also be obtained which have a more uniform colour, and it is interesting to note that it is the material of the vessel in which the sol is made that decides the final colour rather than the nature of the reducing agent or of the dispersion medium. If water in which silver oxide is suspended is treated with hydrogen, it will soon become filled with colloid metal, caused by the reduction of the oxide. This reduction occurs only at the walls of the vessel and not in the solution itself. In a cylinder of ordinary glass the sol will become yellowish brown, but in one of Jena glass, red, violet or blue. It is found that this variety in colour is not caused by any substance dissolved from the glass; for a similar colour is obtained when a vessel made of pure quartz is used. A different result is obtained by using a platinum vessel; in this crystalline silver separates out. The formation of silver mirrors by reduction is also dependent on the nature of the surface on which the separation of the particles of silver takes place.[1]

The fineness of the particles in a solution of colloidal metal and the large surface they develop enable them to react very speedily. This is most evident when they act as catalysts, for example, in the decomposition of hydrogen peroxide by platinum. Even a solution containing only 0·0000028 per cent. of colloidal platinum has a con-

[1] Kohlschütter, *Z. Elektrochem.*, 1908, 14, 49; *Ann.*, 1911, 387, 86.

siderable effect on the peroxide. The catalytic action of the platinum can be lessened or almost entirely stopped by the addition of a very small quantity of foreign substances, which, curiously enough, are the same substances which destroy organic life; the process is termed the poisoning of the catalytic agent. For example, prussic acid hinders the catalysis of hydrogen peroxide by platinum in as low a concentration as $\frac{1}{20,000,000}$ mole per litre; phosphorus reduces the speed to one-eighth in a 0·00004 normal solution; sulphuretted hydrogen, arsenic acid, mercuric chloride and other poisons have a similar effect (Bredig). Many other metallic catalysts are also disturbed by these poisons, but non-metallic catalysts are usually less sensitive to them.

Very highly concentrated colloidal solutions of metals are obtained by the addition of protective colloids before reduction. Paal[1] has successfully made use of two products of albumin hydrolysis, sodium protalbinate and lysalbinate, for this purpose. When these are added to solutions of the salts of platinum, osmium, iridium, palladium, etc., a dark brown or black liquid is formed on reduction by hydrazine. This remains unchanged when evaporated, leaving behind a soluble residue containing up to 70 per cent. of metal. These protected colloids are particularly effective catalytic agents, for the metals, although protected against precipitation, retain their other colloidal properties. For instance, protected as well as compact palladium can absorb hydrogen, and yields a reversible colloid which contains about one atom of hydrogen to every three atoms of palladium. The hydrogen is, however, very readily given up to easily reduced compounds. It therefore acts as a powerful reducing agent, particularly for organic compounds. Thus 1 c.c. of a suitable solution of palladium activates no less than 30 litres of hydrogen for the reduction of nitrobenzene. Another interesting series of protected colloids are the silver colloids of Carey Lea,[2] obtained by reducing a moderately concentrated solution of silver nitrate by means of a solution of ferrous sulphate, sodium citrate and sodium hydroxide. First a violet silver deposit is precipitated, which is repeatedly dispersed in water and precipitated by ammonium nitrate, in order to remove the foreign salts. This silver is dispersed in water, and when evaporated the sol gives a white metallic skin of silver which redisperses in water. Another form which cannot be redispersed in water, but which is interesting on account of its golden colour, is obtained by a similar reduction, using tartrate instead of citrate. This is entirely stable when motionless, but by continued shaking passes into the white form. This occurred when some specimens were sent a distance by rail, whereas other specimens which had been packed in cotton-wool, in order to prevent shaking

[1] Ber., 1904, 37, and foll. vols.
[2] Amer. J. Sci., 1889, 37, 476.

retained their golden colour. Pressure, heat and light also change the golden into the white form.

Copper is the most electropositive metal which remains stable as a hydrosol even in the presence of a protective colloid; its solutions, obtained by Paal's method or by other means, have various colours.

As already indicated, the behaviour of protected colloidal metals towards precipitants is similar to that of the protective colloids which are added to them. For instance, a gold colloid containing only 3 per cent. of gelatin cannot be precipitated by common salt, but coagulates on the addition of tannic acid, which is a precipitant of gelatin.

The substances produced by the corrosion of metallic tungsten, molybdenum, titanium, thorium, zirconium and silicon are related to the protected colloids. If metallic tungsten is finely powdered and then treated alternately with acids and alkalis it soon forms a colloidal solution. It may be precipitated as a plastic substance which can be forced through a fine gland in the shape of a thread, and in this form was formerly used for the filaments in incandescent lamps. It may be assumed that tungstic acid is the protective colloid (Kuzel).

Sulphur and selenium are the only non-metals which have been intimately studied in colloidal solution. Colloidal sulphur is often produced when polysulphides are dissolved in acids—a fact known to every analyst—or may be produced by the action of sulphuretted hydrogen on sulphur dioxide in water (cf. the polythionates: Wackenroder's solution, p. 562), but the best method is to decompose a concentrated solution of sodium thiosulphate with concentrated sulphuric acid. The colloidal sulphur is amorphous and rather plastic, and can be entirely dissolved in water, yielding a more or less clear yellow liquid, which may contain up to 5·5 per cent. sulphur, but is never free from electrolytes. Bassett and Durrant[1] have shown that colloidal sulphur prepared in this way is the sodium salt of a sulphur-polythionate complex. If an effort is made to get rid of the electrolytes altogether, or if a larger quantity of electrolyte is added to the solution, the sulphur will be precipitated. Hence it is seen that a fixed quantity of electrolyte is essential to the existence of the solution, and must not be exceeded. If the quantity of electrolytes is gradually increased, the larger particles are precipitated first, leaving behind a sol of fine particles. Otherwise the most powerful precipitants are the largest cations, in the following order:

$$Cs > Rb > K > Na > NH_4 > Li > H ;$$
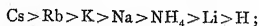
whereas the addition of anions checks the precipitation in the following order:

$$\frac{SO_4}{2} > NO_3 > Cl > Br > I.$$
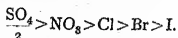
[1] J. Chem. Soc., 1931, 2919.

The sulphur solution does not keep long, but usually separates into crystals of sulphur.

Colloidal selenium is produced as a red solution by the action of sulphur dioxide on selenium dioxide, or by dissolving non-colloidal selenium in hydrazine hydrate. It may also be obtained by oxidising an aqueous solution of selenium hydride with the oxygen of the air or with a few drops of hydrogen peroxide. Selenium is also used to form ruby glasses—pyrosols.

Colloidal graphite or amorphous carbon can be obtained in various ways, but the solutions are not pure and the sol is stabilised by complex carbon compounds.[1] Carbon also forms aerosols in smokes, in which the charged particles are dispersed in air; ammonium chloride, phosphorus pentoxide, arsenic trioxide and many other substances give similar aerosols. The coagulation of carbon smokes gives soot, which may be considered to be the gel of the carbon sol.

The more important colloidal solutions of compounds are discussed with the compounds they contain.

[1] Thorne, *Kolloid. Z.*, 1922, 31, 119.

MODIFICATIONS OF THE ELEMENTS—(B) SPECIAL

Hydrogen, oxygen, nitrogen, halogens—Sulphur, selenium, tellurium—Arsenic, antimony, phosphorus—Boron, silicon—Carbon—Metals

Hydrogen, Oxygen, Sulphur, Nitrogen and the Halogens

The Dissociation of Polyatomic Molecules. — The splitting up of molecules of elements into smaller molecules, or even into atoms, is observed in nearly all the non-metals which can be vaporised. It usually takes place at high temperatures, *e.g.* in iodine (p. 97), and leads to a reversible equilibrium between the products of dissociation and the original molecule. It may also occur through the action of an electrical discharge or of a silent discharge, in which case the rise of temperature plays no part. In the various groups of the periodic system the tendency to decomposition increases with a rise in atomic weight.

The decomposition of the diatomic molecules of the halogens to single atoms was discovered and studied by V. Meyer, who observed that the vapour density is abnormally diminished by a rise of temperature. This indicates that the number of its molecules has increased—they have been split up into smaller particles. The extent of this decomposition can thus be measured if—with atmospheric pressure presumed constant—gases in each condition are reduced to the volume which they would possess at 0°. If the gas has n times the theoretical volume it should attain, the number of its molecules has been increased n times. It was found that above 600° iodine undergoes a greater increase of volume than it should according to Charles' Law. On account of difficulty with the apparatus the temperature at which the volume becomes twice its theoretical value, *i.e.* when the decomposition $I_2 \longrightarrow 2I$ was complete, could not be attained. Meyer used in his investigations the apparatus which is associated with his name. This method led to rather faulty results, for the iodine vapour not only pushes away the air in front of it, but also diffuses into it to a certain extent. Under these conditions the partial pressure of the iodine does not actually equal, but is less than, the atmospheric pressure. In later researches these errors were avoided by determining the pressure of iodine vapour at various

temperatures in absence of air.[1] Using 1·958 millimols of iodine vapour, the quantities of I_2 and I were found to be as follows:

Temperature	200°	800°	900°	1000°	1100°	1200°
Millimols I_2	1·958	1·817	1·707	1·541	1·333	1·113
Millimols $2I$	0·000	0·266	0·484	0·814	1·226	1·662

The bromine molecule is less readily broken up. Decomposition begins at 800°, and at higher temperatures is as follows:

Temperature	800°	850°	900°	950°	1000°	1050°
	0·16	0·65	1·48	2·53	3·98	6·30 per cent. decomposed.

With chlorine the decomposition is still less:

Temperature	1200°	1240°	1280°
	1·50	2·10	3·05 per cent.

The fluorine molecule has so far resisted all attempts to decompose it.

The decomposition calculated by Nernst's heat theorem is a good deal different from that actually found, especially for chlorine. Thus the theoretical temperatures at which a dissociation of 1, 10 and 50 per cent. should be obtained are as follows:

	1%	10%	50%
$Cl_2 \rightleftharpoons 2Cl$	1940°	2270°	2610°
$Br_2 \rightleftharpoons 2Br$	1100°	1320°	1560°
$I_2 \rightleftharpoons 2I$	845°	1060°	1310°

The values calculated[2] from spectroscopic data, using statistical methods, are, however, very much closer to the observed results.

The molecules of the elements in Group VI of the periodic system are commonly made up of eight atoms. When heated, these molecules do not decompose at once into single atoms but give simpler polyatomic molecules. A number of different kinds of these molecules can exist at the same time in the equilibrium mixture. For example, in sulphur the molecules S_8, S_6, S_2, and possibly S_4, all occur together, and rise in temperature increases the proportion of the more highly disintegrated molecules.[3] Decomposition of octatomic sulphur commences at its boiling point, and has already proceeded as far as S_2 at 900°. With a further rise of temperature the molecular weight remains constant; even at 1560° the formula of the sulphur is still S_2, but at very high temperatures a further dissociation into atoms takes place.

Selenium is represented by Se_2 at 900° and 1800°; below 900° the molecules Se_6, and possibly also Se_8, are present. At 2000° decomposition into single atoms begins. The decomposition of oxygen by heat is dealt with later (p. 119).

[1] Starck and Bodenstein, *Z. Elektrochem.*, 1910, 16, 961.
[2] Glasstone, *Ann. Rep. Chem. Soc.*, 1935, 32, 66.
Preuner, *Z. physikal. Chem.*, 1913, 81, 120.

All the tetratomic elements, phosphorus, arsenic and antimony, are known to dissociate, although the phosphorus molecule, as might be expected, is dissociated with difficulty. The dissociation does not begin until 1000°, and at about 1700° is only 50 per cent. Moreover, here three forms of molecules, P_4, P_2, and P_1, have to be reckoned with (Preuner). In arsenic and antimony the splitting takes place more easily, the molecules at the following temperatures having the average atomicity given :

670°	860°	1325°	1437°	1725°	1572°	1640°
As_4	$As_{3.98}$	$As_{3.70}$	$As_{2.62}$	$As_{2.1}$	$Sb_{2.96}$	$Sb_{2.08}$ atoms.

Active Nitrogen.—Nitrogen, the lightest element of this group, has not so far been disintegrated by the action of heat. Its decomposition by means of a spark or glow discharge is very interesting. If pure nitrogen is subjected to a silent electric discharge, it will partly change to the "active" condition; the latter is quite unstable and soon returns to the unexcited state, giving the golden yellow afterglow of nitrogen.[1] This decomposition is facilitated by the presence of a very small quantity (1 : 1000) of another gas, only the rare gases being ineffective. It can be proved that this glow is not caused by gaseous ions, because it is not affected by an electric field. On the other hand, the glow is increased by cooling and decreased by heating; thus the formation of the molecules is facilitated by cooling down (or compression), an indication of a reaction which can be accomplished by a diminution in volume—in other words, a formation of molecules from a larger number of atoms. The change back to the normal state, due to the action of light, does not consist in the mere union of two atoms, although this rapidly follows, if the action of the light persists for a long time. It is rather the formation of an "activated" molecule * in the first place, with the help of an ordinary nitrogen molecule, when the reaction is of the third order (Sponer).

$$2N + N_2 = N_2^* + N_2.$$

It is not certain, however, that the active nitrogen is atomic. E. Willey[2] found that although the heat of formation was negative it was not so great as might be expected for the decomposition $N_2 \longrightarrow 2N$, and consequently suggested that metastable molecules of nitrogen are formed.

Photometric measurements made during compression by Raleigh[3] show that brightness varies as the square of the concentration of active

[1] See Strutt, *Proc. Roy. Soc.*, 1911, 85A, 219; 1913, 88A, 539.
[2] *Nature*, 1926, 117, 381.
[3] *Proc. Roy. Soc.*, 1935, 151 A, 567.

material. This suggests a bimolecular reaction in place of the third order mechanism postulated above. Further, addition of neutral gases to glowing nitrogen does not affect the luminosity, and the time of decay between two standard intensities at constant volume is, at low pressures, almost independent of the pressure.

As a chemical reagent this form of nitrogen is one of the most active of the elements; alkali metals and lithium are converted into azides and with the vapours of metals such as zinc, cadmium and arsenic it gives nitrides, which are decomposed by water or alkali hydroxides with evolution of ammonia. Liquid mercury gives a nitride even at a low temperature; sulphur, carbon disulphide, sulphur chloride and sulphuretted hydrogen all yield nitrogen sulphide N_4S_4. Similarly, active nitrogen reacts with phosphorus, with many metal chlorides (which give a green fluorescence), and even with hydrocarbons of all kinds; in the latter the process is accompanied by the formation of hydrocyanic acid or nitriles.

Oxygen, hydrogen, chlorine, bromine and iodine can all be decomposed into atoms by means of an electric discharge in the gases at low pressures; these atoms are distinguished by special chemical activities whereby an afterglow is produced, at any rate in the case of oxygen. If the quantity of atomic oxygen is calculated from the heating effect due to recombination on a platinum wire, as much as 20 per cent. may be present in oxygen which has been subjected to the silent electric discharge. The gas contains no ozone, though when condensed in liquid nitrogen some can be detected. The atomic oxygen reacts very slightly with hydrogen, only 2 per cent. of the collisions with H_2 being effective; CO reacts only to the extent of 5 per cent., but HBr is completely split up into water and halogen; HCl, however, reacts only to the extent of 25 per cent. The complete reaction with H_2S gives S, SO_2, SO_3 and H_2SO_4, while CS_2 gives a mixture of CO, CO_2 and SO_2. With ammonia a 25 per cent. reaction gives an unknown compound which explodes spontaneously. Curiously enough, atomic oxygen reduces MoO_3—the white oxide formed is not further reduced by hydrogen.[1]

Hydrogen.—The decomposition of hydrogen by heat has been demonstrated in the following manner: the amount of heat lost by a glowing wire owing to convection can be calculated for any kind of gas surrounding it. These calculations were confirmed by experiments in mercury vapour, nitrogen, carbon monoxide and arsenic up to very high temperatures, but not in hydrogen above 2000° absolute. As the withdrawal of heat in hydrogen is greater than is to be expected from the theory, Langmuir [2] has concluded that the loss of heat is occasioned by the energy expended in the splitting up of the

[1] Harteck and Kopsch, *Z. Elektrochem.*, 1930, 36, 714.
[2] *Z. Elektrochem.*, 1914, 20, 498 ; 1917, 23, 217.

molecules, and the splitting is facilitated by decreased pressure. The percentage decomposition is as follows:

Absolute temperature .	2000°	2300°	2500°	3100°	3500°	4000°
At 760 mm., per cent. .	0·33	1·4	3·1	17	34	61
At 1 mm., per cent.	8·7	32·8	57·5	96	99·3	99·9

Atomic hydrogen can also be prepared from H_2 at 0·3 mm. pressure with an alternating current of 0·5 amp. at 5000 volts; these are the conditions under which the lines of the Balmer series, known on theoretical grounds to be due to atomic hydrogen, are strongly developed.[1]

On account of its low atomic weight the atomic hydrogen very easily diffuses to the cool walls of a vessel and is adsorbed on them; it there combines to H_2 and reappears as such on warming. This action of the walls of the vessel is greatly diminished if they are coated with water, or best with syrupy phosphoric acid. There is proof that ionised molecules are not present, because the hydrogen is not influenced by an electric field. It is highly active; it converts unsaturated hydrocarbons into the corresponding saturated compounds, forms hydrides with S, Te, P, As, Sb, Ge and Sn, and with chlorine gives HCl even in the dark. LiH, NaH and KH result from the reaction of the metals at room temperature,[2] and Pietsch and his co-workers[3] have prepared solid hydrides of Cu, Ag, Au, Be, Ga, In and Ta. With O_2 and CO, two atoms of hydrogen are attached, giving $H.O.O.H$ and $H.CO.H$ respectively. HBr is oxidised by the removal of its hydrogen atom: $H + HBr \longrightarrow H_2 + Br.$ Oxides, even WO_3, and salts are reduced to the metal, and the metal thus formed is catalytically active and frequently becomes heated in causing the recombination of the hydrogen atoms to the diatomic form. This occurs when mirrors of Bi, Zn and Cd are exposed to a stream of the gas; the mirrors move along the tube. The movement is not due to hydride formation but to distillation of the metal, the necessary heat for the process being supplied by the exothermic conversion $2H = H_2 + 98$ Cals. This action is largely parallel to that of metal electrodes in the phenomena of overvoltage, for metals with high overvoltage (Au, Hg, Pb) have little catalytic action, while those with low overvoltage (Pt, Pd, Ni) have a greater effect.[4] It is curious that atomic hydrogen does not form ammonia with molecular nitrogen; it may be concluded that in the synthesis of ammonia the nitrogen as well as the hydrogen must be activated.

[1] Wood, *Proc. Roy. Soc.*, 1920 [A], **97**, 455 : 1922, **102**, 1 ; Pearson, Robinson and Stoddart, *ibid.*, 1933 [A], **143**, 275.

[2] Ferrell, Pearson and Robinson, *J. Chem. Soc.*, 1934, 7.

[3] *Naturwiss.*, 1931, **19**, 573, 574, 737 ; *Z. Elektrochem.*, 1933, **39**, 577 ; *Kolloid Z.*, 1934, **68**, 226.

[4] Bonhoeffer, *Z. physikal. Chem.*, 1924, **113**, 199, 492 ; 1926, **119**, 385, 474.

The great heat of recombination to ordinary hydrogen can be utilised for welding. If hydrogen is blown through an electric arc between tungsten poles, a considerable proportion is converted into the atomic form. In this "atomic hydrogen flame" tungsten, tantalum and thorium dioxide are readily melted, the temperature being higher than that of the oxy-acetylene flame.[1]

The life period of the hydrogen atom has been determined by Bonhoeffer by finding the quantity of atomic hydrogen with varying rates of flow indicated as H_2S by the action on sulphur placed at a distance from the source of the active hydrogen. He found that the half mean life period of the H atom was $\frac{1}{3}$ sec. at 0·5 mm. pressure.

It has always been supposed that nascent hydrogen was in the atomic state. H. S. Taylor[2] has brought forward a proof of this, as he found that 90 per cent. of the hydrogen liberated at a cathode was converted into hydrogen peroxide when oxygen at 100 atmospheres pressure was allowed to stream over the pole.

The hydrogen occluded on platinum or palladium may be regarded as atomic, for it reduces chlorine and iodine to their hydrides, converts mercuric into mercurous chloride, and precipitates noble metals from solutions of their salts. This behaviour is not entirely contradictory to the catalytic action of platinum in causing recombination of atoms, since the latter may remain adsorbed up to a certain saturation point.

Ordinary hydrogen, H_2, is a mixture of ortho- and para- forms. This was first predicted theoretically and then soon after discovered practically; *para-* and *ortho-hydrogen*[3] are present in the ordinary gas in the proportions 1 : 3 which is the limiting value which can be attained. The nuclei of the two atoms in the hydrogen molecule have a spin like that of the earth on its axis, the rotation being in the same direction for both in orthohydrogen, in opposite directions in parahydrogen. There is consequently a difference in certain physical properties, particularly in heat of rotation of the molecules, which shows as marked differences in specific heat at low temperatures. The two forms persist under certain conditions in which spectra are excited; for example, the lines constituting the bands in the spectrum of molecular hydrogen show alternating intensities, due to the 1 : 3 ratio of the two varieties. There are slight differences in melting point and boiling point.

	Ordinary H_2	Para-H_2	Ortho-H_2	
Melting point . . .	13·95	13·82	13·99	°*T.*
Boiling point (at 760 mm.)	20·39	20·26	20·43	°*T.*

In mixtures of ortho- and para-hydrogen the equilibrium is rapidly shifted almost entirely to parahydrogen by adsorption of the hydrogen

[1] I. Langmuir, *Gen. Electric Rev.*, 1926, **29**, 153.

[2] *J. Amer. Chem. Soc.*, 1926, **48**, 2845.

[3] Bonhoeffer, Harteck and Eucken, *Naturwissen.*, 1929, **17**, 182, 321.

on charcoal, or on nickel deposited on Kieselguhr, at the temperature of liquid hydrogen; the change is also accelerated by increase in pressure. Practically pure gaseous para-hydrogen is obtained by allowing the hydrogen adsorbed on charcoal to evaporate at the temperature of liquid hydrogen. The para- form should be the sole variety at absolute zero, conversion to increasing amounts of ortho-, up to 1 : 3 limit, proceeding as the temperature is raised. Para-hydrogen takes some time to revert to the usual mixture; it is fairly stable for some weeks at ordinary temperatures, in glass vessels, but the change is rapidly effected by oxygen, NO and NO_2, all of which are paramagnetic; diamagnetic gases (N_2O_4, N_2, N_2O, SO_2) are without effect. Aqueous solutions containing paramagnetic ions (e.g. $Mn^{..}$, $Fe^{..}$, $Co^{..}$, $Ni^{..}$, $Cu^{..}$) accelerate the change; but not $Zn^{..}$ solutions (diamagnetic). The change is also catalysed by metals, which adsorb hydrogen atom by atom and on recombination the ordinary form naturally reappears[1]; platinised asbestos causes it to take place immediately and the electric discharge effects rapid transformation. Catalysis by platinum is subject to the usual poisoning effects and is hastened by the presence of oxygen. The change proceeds readily as a homogeneous reaction of order 1·5 in quartz vessels at temperatures of 600° and above, a result which accords with the mechanism

$$\text{para-}H_2 + H \rightleftharpoons \text{ortho-}H_2 + H$$

in which atomic hydrogen is involved in the change.

Deuterium is also a mixture of ortho- and para- forms. At room temperature it consists of two parts ortho- and one part para-. At low temperature and with catalysts, such as charcoal or nickel, pure ortho- is obtained, which reverts slowly to the equilibrium mixture at room temperature; as in ortho- and para-hydrogen, oxygen catalyses the change, but less rapidly.[2]

Recombination of the Products of Dissociation.—The labile dissociation products formed at high temperatures or by the action of the electric discharge do not necessarily give the original molecules when they recombine. On the contrary, it is possible for other bodies to appear which, although more stable than free atoms, are more labile than the original molecules. These frequently represent a more highly polymerised product than the common molecules, such as triatomic nitrogen N_3, triatomic oxygen O_3, etc. The best known and most stable of these products is ozone, O_3. Its constitution can be represented by a ring-shaped combination of three oxygen atoms; it may perhaps also form an open chain. It is even possible that

[1] Farkas, *Z. physikal. Chem.*, 1931, **14B**, 371.

[2] A. Farkas, L. Farkas and P. Harteck, *Science*, 1934, **79**, 204; Clusius and Bartholomé, *Z. physikal. Chem.*, 1935, **29 B**, 162.

four atoms may combine to form one labile molecule[1] (oxozone). Trautz[2] has shown that atomic nitrogen when transformed first produces triatomic nitrogen, N_3, particularly at low temperatures; which indicates that a single atom has united with a molecule of nitrogen, N_2, rather than that three atoms have combined—$N_2 + N = N_3$. This is proved by observing the speed of the reaction. On account of the rapidity with which triatomic nitrogen decomposes it has not yet been possible to investigate the differences between the chemical properties of triatomic and monatomic nitrogen.

Triatomic hydrogen, H_3 (hyzone), appears to be rather more stable, at least in the form of its positive ion H_3^+, first observed by J. J. Thomson in canal rays. This is produced when a glow discharge is passed through a mixture of H_2 and some water vapour, with a fall in potential at the cathode of 3000-8000 volts.[3] It was formerly supposed that this ionised form could exist for a considerable time, but Paneth, Klever and Peters[4] have found otherwise, and state that it cannot be obtained except under the special conditions which obtain in the X-ray tube. Proof is also lacking for the existence of the transitory uncharged H_3. The isotope $_1^3H$ of hydrogen, named tritium, has also been discovered (see pp. 79, 159).

Ozone. — *Formation* (*cf.* p. 97). — In ozone, O_3, we have an unstable polymeric condition of the elementary atom; this example has been longest known and most thoroughly investigated. It is usually produced by the use of electricity; it can be obtained only with difficulty by the thermal disintegration of the oxygen into its atoms (*cf.* p. 98), as it is a strongly endothermic compound; 29.6 Cal. is required to produce one g.-mol. from molecular oxygen. The following are the calculated quantities in the $3O_2 \rightleftharpoons 2O_3$ equilibrium:

Absolute temperature	1569°	2321°	4773°
Weight per cent. O_3.	0.15	1.52	16.50
Volume per cent. O_3.	0.1	1.0	10.0

It may therefore be anticipated that if ozone is cooled an almost total decomposition will take place. The rate of the decomposition, however, is diminished with fall in temperature, as is usual in most reactions, and ozone is therefore more stable at room temperature; with only a slight rise, however, decomposition takes place very rapidly, so that at 300° ozone can no longer be detected. Catalysts such as platinum black or metallic oxides, as well as metallic walls of vessels, destroy it very quickly, even at a low temperature; even liquid

[1] G. N. Lewis, *J. Amer. Chem. Soc.*, 1924, 46, 2027.
[2] *Z. Elektrochem.*, 1919, 25, 297.
[3] Stark, *Z. Elektrochem.*, 1913, 19, 862.
[4] *Z. Elektrochem.*, 1927, 33, 102.

ozone can be decomposed in a moment with spontaneous explosion. The decomposition of ozone is also catalysed by chlorine; the process is complex and chain reactions are probably involved.

The thermal production of ozone is successful if the air or oxygen is caused to pass over a highly heated surface (a glowing Nernst filament) or blown through a hydrogen flame. Below a certain velocity no trace of ozone is obtained, but only nitric oxide or, when the air is damp, hydrogen peroxide; the point at which the transformation occurs is rather sharply defined; for instance, in one experiment, with a wind velocity of 5·2 m./sec. there was a great preponderance of nitric oxide—at 5·5 m./sec. a similar preponderance of ozone. The quantity of ozone obtained in this manner is not great, for even at the prevailing temperature, and supposing that equilibrium is attained, little more than 0·1 per cent. ozone could be expected. Complete equilibrium is not, however, reached, because only a small amount of the air can be brought into direct contact with the heated surface. A more satisfactory method, which allows of better cooling and a richer yield of ozone, consists in causing a platinum wire or filament to become incandescent in liquid air or oxygen; the ozone formed dissolves in the liquid and reaches the cooler parts, where it is retained, while in the neighbourhood of the glowing body the air, which boils more readily than ozone, goes on steadily evaporating. The concentration of the ozone is then merely a question of time, but it is impossible to obtain 100 per cent. ozone in this manner, for a certain amount always returns to the heated area, and is again converted into the original oxygen. This method of production is not economical.[1]

Ozone is produced by chemical means when atomic oxygen is formed at low temperatures, and in the absence of easily oxidised substances. The decomposition of periodic acid by heat, which occurs at 130°, produces oxygen which is rich in ozone. The most favourable condition for retaining ozone is when the atomic oxygen is produced at room temperature. For instance, when water is decomposed by fluorine, $F_2 + H_2O \longrightarrow 2HF + O$, a reaction which takes place at a low temperature, the ozone formed from the oxygen atoms may be preserved. At room temperature the formation of atomic oxygen also takes place during the auto-decomposition of hydrogen peroxide, as well as of many per-acids. Thus ozone is obtained in treating barium or sodium peroxide, potassium permanganate, dichromate, persulphate or percarbonate, etc., with cold concentrated sulphuric acid. The per-acid which is first produced easily decomposes in the absence of water.

Ozone can also be obtained by the electrolytic production of oxygen

[1] Franz Fischer, Braehmer and Marx, *Ber.*, 1906, 39, 940, 2557; 1907, 40, 443, 1111, 3631.

atoms. Here also all reactions which tend to use up the free atoms or to induce a secondary decomposition of the ozone must be avoided, as in a purely chemical method of preparation. The ozone does not remain unchanged during the electrolysis of acidified water with electrodes of carbon or of base metals, for they are oxidised by the free oxygen atoms as well as by the ozone. When electrodes of a noble metal such as platinum or gold are used, ozone is formed; even lead is serviceable, as it becomes covered with a layer of lead oxide and is then immune from attack. Twenty per cent. sulphuric acid is a good electrolyte to use, though hydrofluoric acid is better. A higher concentration of ozone may be obtained by using a high current density and by well cooling both electrolyte and electrodes.

An interesting method of forming ozone is by the action of moist air on phosphorus. This is a secondary effect of the oxidation of the phosphorus, and is checked by conditions which produce a negative catalysis of the main reaction: e.g. low temperature, or the presence of certain substances such as unsaturated hydrocarbons, etc., which in the absence of air themselves react with phosphorus.[1]

The use of electric discharges of all kinds is a more satisfactory method of producing ozone. It is formed when electric sparks are passed through air or oxygen, also by electric induction, or silent discharges; the odour of ozone in the spark discharges of the electrical machine is well known. Ozone is best obtained in large quantities by passing oxygen between two concentric glass cylinders, the narrower of which is lined inside, and the wider one outside, with tinfoil. A high potential difference is maintained between the layers, and by this means a yield of 14 per cent. ozone is readily secured. The attainment of a state of equilibrium is the chief aim, for an increase in the quantity of electricity supplied does not increase the yield.

Ozone is also formed by the action of rays of various kinds on oxygen, as for instance radium and cathode rays, but more especially by the irradiation of the air with ultra-violet rays. For this reason it is found in the upper layers of the atmosphere (the whole quantity of ozone in the air is equal to a layer of gas 3 mm. thick—London air contains only $1 \cdot 1 \times 10^{-6}$ vol. per cent.) and also very obviously in the neighbourhood of mercury vapour lamps.

Properties.—Ozone is a bluish gas, with a very characteristic odour; when compressed it becomes indigo blue. It is blue-black when liquid, and forms a dark violet crystalline mass when solid. It is almost insoluble in water, but dissolves easily in carbon tetrachloride, glacial acetic acid, and more particularly in liquid nitrogen, forming blue solutions. It is remarkable that liquid oxygen and liquid ozone do not mix in all proportions. The melting point of ozone is $-251 \cdot 4°$,

[1] Willstätter and Sonnenfeld, *Ber.*, 1914, 41, 2801.

the boiling point $-111.5°$. Explosions occur when liquid ozone boils away, and in all states it is highly explosive under pressure variations or percussion. From the density of the gas its molecular weight is found[1] to be 48 (O_3).

The chemical nature of ozone is determined—first, by its ability to split up into free atoms of oxygen, which makes it a very powerful oxidising agent; and secondly by its power of attaching itself as a complete molecule to different bodies—for example, to organic substances having double bonds.

Oxidation by ozone usually takes place by the action of one atom of oxygen from the ozone molecule, thus leaving behind a molecule of oxygen. The oxidising action is similar to that produced by more powerful agents, such as chlorine or the higher oxides of nitrogen; this has frequently caused confusion, the supposed ozone being in reality one of the other oxidising agents. Thus the liberation of iodine from potassium iodide, the bleaching of indigo and other similar reactions, are not characteristic of ozone, for other oxidising agents give them as well. On the other hand, the blackening of silver foil by the formation of a peroxide, Ag_2O_2, is a reaction peculiar to ozone, and is most visible at a fairly high temperature; at 240° it appears very readily, but disappears at a red heat, or when left for some time, when it will commence to turn blue. At room temperature the reaction can only take place quickly with silver which has been corroded with acid, or rendered impure by the addition of a small quantity of metallic oxides; a sufficient amount of iron may be added by rubbing with rusty emery paper. If, however, the silver was blackened at 240° it will have undergone so great a change that after the peroxide has been decomposed, at red heat, the silver will henceforth produce the ozone reaction at room temperature. Liquid ozone also tarnishes silver, but the black colour soon fades.[2]

The effect of ozone on mercury is also characteristic; the metal loses its mobility when it is subjected to a stream of ozone, owing to the formation of a thin skin of mercurous oxide. The mercury curdles on the surface and clings to the sides of its vessel. This reaction also has its optimum temperature, which is about 170°; here the reaction produces thick brown fumes. The mercury regains its original properties if left for a short time at room temperature.

In their instability these oxides of silver and mercury show a certain likeness to the products obtained by the action of ozone on alkali hydroxides. The brown salts of ozonic acid (p. 417) produced by the action of a stream of ozone on solid potassium or rubidium hydroxides are transformed into alkali hydroxides at room temperature. Similarly, if a stream of ozone is passed into liquid ammonia an orange colour

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[1] Ladenburg, *Ber.*, 1910, 43, 631.

[2] Manchot and Kampschulte, *Ber.*, 1907, 40, 2891.

is obtained, caused by the production of an ozonide; oxidation soon takes place with formation of ammonium nitrite and nitrate.

Several indicators can be employed for the detection of ozone. Potassium iodide-starch paper cannot be used by itself for this purpose, because several other oxidising agents also turn it blue, but, in conjunction with phenolphthalein, it may be used, as the latter becomes reddened by the action of ozone (or hydrogen peroxide). Unlike other oxidising agents such as chlorine, it is unable to combine with the potassium hydroxide formed by the decomposition of the aqueous potassium iodide, which consequently turns alkaline. The brown colour, Tl_2O_3, produced with thallous hydroxide paper, is more visible, like the blue colour produced with guaiacum tincture, but these can also be produced by numerous other oxidising agents. On the other hand, an excellent indicator for distinguishing various oxidising substances is the so-called "tetra-base" paper which is soaked in an alcoholic solution of tetra-methyldiaminodiphenylmethane: $(CH_3)_2N \cdot C_6H_4 \cdot CH_2 \cdot C_6H_4 \cdot N(CH_3)_2$; when used moist it undergoes the following changes:

With:	Ozone	NO_2	Cl_2 or Br_2	H_2O_2
	violet	straw yellow	blue	remains colourless.

These reactions are especially delicate in the presence of a small quantity of free acetic acid.[1]

The addition of ozone at double bonds has so far been observed only in organic substances, so it need only be briefly mentioned here. This reaction, which according to Harries occurs in the following manner,

$$>C=C< \ + \ O_3 \ \longrightarrow \ \begin{array}{c} >C-C< \\ | \ \ \ | \\ O \ \ \ O \\ \diagdown \diagup \\ O \end{array} \ ,$$
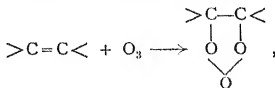
has become of special importance, chiefly because of the disintegration of the ozonides at the place where the double bond was originally situated. It is thus possible to obtain a valuable insight into the constitution of such organic substances. Harries' researches showed also that the polymerisation of oxygen is apparently not exhausted when three atoms have combined, but that it is even possible for a tetratomic molecule to be formed. According to Harries, O_4 or, as he called it, "oxozone" is present in highly ozonised oxygen; e.g. in oxygen containing 11-14 per cent. of ozone, and can be removed by washing with sodium hydroxide and concentrated sulphuric acid.[2] In unsaturated compounds, in addition to ozonides which contain O_3, unwashed ozone produces oxozonides which have one more atom of oxygen; immediately the ozone is washed in the manner described above, only the ozonides are formed. Harries found that the quantity of oxozone contained in ozone is about one-third; hence the isolation of oxozone might be expected by fractional distillation of the liquefied gas. This cannot be done, and as it has been found impossible to isolate oxozone,

[1] Arnold and Mentzel, *Ber.*, 1902, 35, 1324.

[2] Harries, *Ber.*, 1912, 45, 936.

its existence is doubtful,[1] but Guillien[2] from a study of changes in absorption band intensities of liquid oxygen has found evidence for O_4.

Sulphur, Selenium, and Tellurium

No other element has so many different modifications as sulphur, except possibly selenium—but up to now the latter has not been much investigated. Not only do the molecules of sulphur vary by reason of the difference in the number of atoms which they contain, but even when the number of atoms appears to be the same, their orientation in the molecule may differ so that both primary and secondary modifications exist.

Sulphur.—The molecular size and distinct properties of the following are known :

(1) $S\lambda = S_8$. Exists in two enantiotropic forms : rhombic sulphur and monoclinic sulphur (p. 95).

(2) $S\rho = S_6$. Engel's sulphur (S.E.). Occurs in slow reactions when the atomic form separates first.

(3) $S\pi = S_4$. "Crumbly" sulphur of Magnus-Aten. Produced by the thermal disintegration of S_8; most plentiful at about 200°.

(4) A series of other forms of crystallised sulphur, some shining, like mother-of-pearl, and monoclinic, some triclinic, etc.; these have not yet been sufficiently investigated to allow of their being included in a series with any certainty.

Besides the crystalline forms having definite molecular weights, there exist others which are amorphous and of unknown structure; these fall into two divisions :

(5) $S\mu$. The amorphous sulphur insoluble in carbon disulphide.

(6) Numerous forms of amorphous sulphur more or less soluble in carbon disulphide, which possess various properties and consist of mixtures or undercooled melts of one of the forms of sulphur mentioned above.[3]

In the two forms of S_8 the conditions are very simple. If rhombic sulphur (a-sulphur), obtained either in the natural state or crystallised from carbon disulphide, is heated to 95·6° or above, it changes into the monoclinic β-form, which reverts on being cooled. β-sulphur has a greater volume than a-sulphur, and therefore if it is subjected to pressure at its transformation point it will change into a-sulphur. If the pressure is raised by one atmosphere, the transformation point will correspondingly be raised by 0·05°. Both these changes—that of a- into β-sulphur as well as the reverse process—are effected slowly in the solid state; and at temperatures which are far removed from the transformation point

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[1] Riesenfeld and Schwab, *Ber.*, 1922, **55**, 2088.

[2] *Compt. rend.*, 1934, **198**, 1486.

[3] See S. R. Das, *Indian J. Physics*, 1938, **12**, 163.

the changes may take days to complete, but the speed is greatly increased by friction after inoculation. The change from a- to β-sulphur takes place very quickly from the liquid condition ; if sulphur is heated slightly above its melting point and is then left to crystallise in the container, after piercing the skin of solidified sulphur which has formed on the surface and pouring out the liquid contents of the crucible, beautiful crystals of monoclinic β-sulphur will be found adhering to the sides, which, by their long needle-like form, pliability and pale yellow colour, can be distinguished at a glance from the compact, brittle and " sulphur-yellow " crystals of the a-sulphur. The formation of β-sulphur from the fused mass does not take place directly but *via* a transient, intermediate monotropic phase. The molecular weight of both forms of sulphur is found to correspond to the formula S_8, by determining the lowering of the freezing point in various solvents, or the rise of the boiling point above and below the transformation point.

In investigating this transition point and other physical properties, sulphur must not be heated too high above its melting point. Above this point it changes into other molecular forms, the successive appearance of which can easily be recognised. Sulphur forms a mobile, light yellow liquid, but just above the melting point becomes gradually thicker until it is sticky and dark brown, and only becomes a thin liquid again at a higher temperature. The maximum viscosity occurs at about 200°. The forms of sulphur which cause this abnormality are the modifications $S\pi(S_4)$ and insoluble amorphous sulphur. They persist for some time after cooling, and it is due to them that the physical properties of cooled sulphur, as well as the transformation point of monoclinic into rhombic sulphur, differ according to the thermal history of the sample. The duration of the alteration is greater when the heating to which the sulphur has been previously subjected is prolonged and is carried out at high temperature, for the quantity of the new forms of sulphur is thereby increased.

Another fact which is important for the identification of the modification $S\pi(S_4)$ is that a saturated solution of sulphur in S_2Cl_2, when temporarily heated to 170°, becomes unsaturated, and a further quantity of sulphur may subsequently be dissolved after cooling. It is recognised that this change takes place without the presence of a solvent, because sulphur which has been heated alone to 170° exhibits this increased solubility in all solvents (carbon disulphide, toluene, sulphur chloride) after having been cooled down.[1]

The isolation of $S\pi$ can be carried out by taking advantage of this behaviour. $S\lambda(S_8)$ is practically insoluble in carbon disulphide at $-80°$, whereas $S\pi(S_4)$ is easily soluble at this temperature, and if the solution is evaporated at a very low temperature a particularly yellow form of sulphur remains. Solutions of this form possess a similar

[1] Aten, *Z. physikal. Chem.*, 1913, 81, 257 ; 83, 442 ; 1914, 86, 1 ; 88, 371.

colour, and the lowering of the freezing point indicates the formula S_4. This form remains stable for a time, but gradually changes into insoluble amorphous sulphur ($S\mu$) which later on becomes $S\lambda(S_8)$, the quantity of which increases with time. At any time the amount of the three forms of sulphur present may be determined, for only $S\pi$ is soluble in carbon disulphide at $-80°$; $S\lambda$ dissolves as well at room temperature, so that finally only $S\mu$ remains. By this means it is also possible to show that all three forms are present simultaneously in sulphur which has been heated above its melting point, and that their relative amounts are dependent on the temperature to which they are heated. The quantities of the different forms of sulphur formed on heating to various temperatures are given in the following table :—

Temperature.	$S\mu$ (amorphl.).	$S\pi(S_4)$.	$S\lambda(S_8)$.
120°	0·1	3·6	96·3
140°	1·3	5·0	93·7
170°	13·3	5·8	80·9
196°	28·6	6·3	65·1
220°	32·2	5·3	62·7
445°	36·9	4·0	59·1

It can be seen that the quantity of $S\lambda$ decreases regularly with rise of temperature, while that of $S\mu$ increases. $S\pi$ is present in maximum quantity at 200°: the presence of this form increases the viscosity of the molten sulphur, while that of $S\mu$ reduces it. The very high viscosity of sulphur at 200° is probably due to the $S\pi$ forming a colloidal solution with the other forms as the liquid medium.[1] X-ray examination [2] shows that rhombic sulphur consists of 8-membered rings of sulphur atoms, lying in 2 planes, as indicated in Figs. 27 and 28. The conversion to plastic sulphur is considered to be due to the rupture of these rings and the formation of a long chain [3] (Fig. 29).
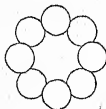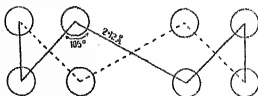
FIG. 27.   FIG. 28.

Thus, with this element a series of dynamic allotropic forms is obtained. As a result the physical data obtained for sulphur are very

[1] Cf. D. L. Hammick, J. Chem. Soc., 1926, 1995 ; 1930, 273.
[2] Warren and Burwell, J. Chem. Physics, 1935, 3, 6.
[3] Meyer and Go, Helv. Chim. Acta, 1934, 17, 1081.

variable; *e.g.* the melting point. Whereas the actual freezing point of monoclinic sulphur (Sλ) is 119·25° it melts below this temperature owing to the presence of S$_4$ and S$_8$. It is even possible to calculate the quantity of Sπ from the depression of the melting point.[1] Since the equilibrium between Sλ and Sπ is not attained at once, some time must be allowed for the temperature to drop, and it is not until a certain point has been reached, about 112°, that the equilibrium between them is reached. (Traces of H$_2$S, SO$_9$, and H$_2$SO$_4$, which are difficult to remove, also affect the properties of sulphur.) Sμ immediately undergoes transformation on melting, giving an equilibrium mixture of Sλ and Sπ.

Sλ(S$_9$) is also obtained by heating Sμ and Sπ(S$_4$), the latter giving first Sμ which passes later into Sλ. Sμ, however, gives Sλ and Sπ, but only Sλ at low temperatures, when little Sπ is present in the mixture.

The modification S$_6$(Sρ), Engel's sulphur, does not take part in the equilibrium of the several allotropic forms of sulphur, but is produced by the decomposition of various compounds of the element, with slow deposition of sulphur; *e.g.* when an acid diffuses into a solution of sodium thiosulphate. The sulphur thus obtained is extracted with chloroform, and on evaporation small leaflets are obtained which are stable for one hour, but which then pass into Sλ(S$_8$) and Sπ(S$_4$). The molecular

Fig. 29.

weight of this allotrope in carbon disulphide solution is expressed by the formula S$_6$; it is thus not identical with Sπ, and is about four times as stable. Its orange-yellow colour is intermediate between that of the forms Sπ and Sλ, as is also the solubility.

The molecular weight of amorphous sulphur, Sμ, which is insoluble in carbon disulphide, is unknown. This form occurs, as has been mentioned, as a transformation product of Sπ and Sρ, as well as in the fused Sλ. It is also formed from Sλ in the cold when the solution is illuminated by sunlight. In the absence of this source of energy the Sμ changes more or less rapidly to Sλ again, all the insoluble sulphur becoming soluble after a time. In view of the fact that at higher temperatures liquid sulphur is richer in Sμ (see table, p. 126), it is obvious that the Sμ will be formed by cooling sulphur vapour. This can be carried out by passing the vapour into water, but air cooling will usually suffice, and "flowers of sulphur," rich in Sμ, are obtained. In the same way it is produced by the incomplete combustion of sulphur compounds, such as sulphuretted hydrogen or carbon disulphide, when the unburnt sulphur is vaporised owing to the heat of reaction, and forms Sμ on cooling. When, however, the sulphur becomes liquid before crystallisation, the Sμ is only found in
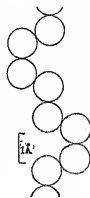
[1] Beckmann, *Z. anorg. Chem.*, 1918, 103, 189.

equilibrium with the other forms of sulphur as in the above table, so that the solidified product is partially soluble in carbon disulphide.

Many modifications of sulphur which are partially soluble in carbon disulphide can be prepared, but all are mixtures. This is true of the so-called "milk of sulphur," which is obtained by the decomposition of a polysulphide solution with acids. It contains a little insoluble sulphur mixed with an excess of the soluble varieties.

Plastic sulphur is produced by pouring viscous melted sulphur into cold water; it is at first a clear viscid liquid, but crystals form in a day or two, and it becomes brittle and fragile. A homogeneous form of sulphur cannot readily be obtained by undercooling, but admixture of foreign substances is known to reduce the rate of crystallisation. The mixture of Sλ, Sπ and Sμ, which is present in plastic sulphur, becomes crystallisable owing to the disappearance of Sπ and of some of the Sμ. The properties of these mixtures are due to the presence of amorphous forms which are only partially soluble in carbon disulphide.

The formation of allotropes with varying molecular weight is the cause of the colour changes which are observed when sulphur is heated. It melts to a pale yellow liquid, but even at 50° above the melting point it has assumed a dark brown tint. Further heating does not greatly increase the depth of colour; the vapour is brownish red. The colour of solid sulphur gets less intense when it is cooled and Sλ is practically colourless at −50°.

Selenium.—The allotropes of selenium appear to be largely analogous to those of sulphur, but they have not been so fully investigated. Besides the metallic or grey form of selenium (which is not represented in the sulphur series), red forms of selenium exist, and although they are not isomorphous with yellow sulphur they are otherwise very much like it. A solution of selenium in molten sulphur gives mixed monoclinic crystals on cooling. The mixtures of the several forms of selenium are as characteristic in properties as those of the yellow forms of sulphur, and are described as liquid, glassy or amorphous selenium. Liquid or glassy selenium is produced when one of the other forms of the element is heated above the melting point. No well-defined freezing point is obtained, but on prolonged cooling the fused mass gradually thickens until at about 40°-50° the glassy consistency is reached; it is then brittle and exhibits a conchoidal fracture. The mass has a dark lead-grey, lustrous appearance, but in thin scales or in powder it is brownish red. This form, in contrast to the sulphur mixtures, undergoes gradual transformation only at higher temperatures. At about 90° it is rapidly changed into a more stable form of selenium—the metallic form, with evolution of heat. The vitreous modification appears to retain a slight quantity of the red form, as it is very slightly soluble in carbon disulphide.

It is difficult to give a brief summary of the work of Briegleb.[1] He has investigated the complex equilibria between the glassy form, two monoclinic (metalloid) forms and hexagonal (metallic) selenium, all of which are stable to a certain extent at room temperature. Molten selenium contains an equilibrium mixture: $Se_2 \rightleftharpoons 2Se_1$, dissociation being greater the higher the temperature. Pure monoclinic Se_2 crystallises from a CS_2 solution, and on extracting the glassy selenium with CS_2 the Se_2 dissolves, leaving the Se_1.

The amorphous powder which is obtained when selenium is produced by rapid reduction in solution differs from this modification only in the size of the particles. Its colour is intermediate between light and dark red, and on heating it becomes soft like the glassy form.

Crystalline selenium in several orange or dark red modifications is readily soluble in carbon disulphide, and is obtained by the prolonged extraction of the amorphous form with hot carbon disulphide and subsequent evaporation of the solution. It is also formed on the surface of glassy selenium when left for some time at the ordinary room temperature in carbon disulphide. It is an open question whether the amorphous form is already present or whether it originates by the action of the carbon disulphide. These modifications are changed into grey metallic selenium on heating, the light variety at about 110° and the darker at 125°. Grey selenium is thus the most stable of all forms at low temperatures. It is obtained from the melted substance in place of the glassy mass by cooling the thin liquid slowly, and thus allowing time for the gradual change to take place. Selenium appears in this form when slowly sublimed or precipitated. It is an almost black powder with a black streak and gives small laminated crystals on sublimation, or the sublimate may be granular, according to the method of preparation. It is completely insoluble in carbon disulphide, but soluble at higher temperatures in several organic solvents such as naphthalene, aniline and ethyl benzoate.

This form of selenium possesses the remarkable property of having its electrical conductivity increased by light. The molecular weight in solution is given by the formula Se_8, probably owing to colloidal aggregation of smaller molecules, but in fused iodine, sulphur, sulphur compounds or some mercury salts there is much dissociation and the value fluctuates according to the dilution[2] between Se_2 and Se_1.

Tellurium.—The properties of tellurium are also dependent upon its preparation, history and thermal treatment. Like sulphur, it exhibits dynamic allotropy (Cohen), but a tin-white form with almost metallic properties is most common. A brown form is also obtained by precipitation at all investigated temperatures. The commoner form

[1] Z. physikal. Chem., 1929, 144, 321, 350.
[2] Olivari, Atti R. Accad. Lincei, (5), 1908, 17 ; 1909, 18 ; 1912, 21 ; Beckmann and Platzmann, Z. anorg. Chem., 1913, 102, 215.

is crystalline and very brittle, and readily sublimes in beautiful crystals *in vacuo* far below its melting point.

Arsenic, Antimony and Phosphorus

These elements each form two monotropic allotropes, but all three elements give intermediate forms which differ markedly from the limiting forms and were long thought to be separate modifications. They have recently been shown to be either one of the chief allotropes in a different degree of dispersity or else solid (colloidal) solutions of one form in another, the proportions being regulated by the rules of dynamic allotropy. It seems likely that both effects occur together, as in phosphorus, where the solid solutions of the white variety in the violet have a different dispersity at different concentrations.

Arsenic.—The relations of the two forms of arsenic are clearer than those of antimony and phosphorus.[1] The chief forms of this element are metallic arsenic, which forms bright, silvery, brittle, hexagonal crystals, of density 5·73, and yellow arsenic, which crystallises in the regular system and is soft, with the remarkably low density of 1·97. Besides these, a grey and a brown to velvet-black form have been described, the former being always produced before the formation of yellow arsenic under the influence of heat or light, whereas the brown form occurs in the separation of arsenic from arsenical compounds in the presence of solvents. The arsenic mirror is produced when the solvent is gaseous. The grey and brown modifications possess no crystalline form, and the appearance and density, according to Kohlschütter, are not constant, because they are only characteristic of the state of subdivision of the material as determined by the conditions under which it is formed. The properties lie, however, between those of the two limiting forms.

The considerable difference in density between the yellow and metallic varieties of arsenic indicates a profound difference in the packing of the particles in the two forms; when a rigid crystal of yellow arsenic rearranges itself into the stable form a different space lattice is produced, and in solution nascent arsenic atoms unite to form molecules of stable arsenic.

The yellow form of arsenic is the most unstable, and as a monotropic modification is produced only from the vapour of the element. The vapour of the arsenic can be passed into well cooled carbon disulphide, which absorbs it readily, and on cooling to −70° or on evaporation the yellow rhombohedra of this modification of arsenic crystallise out. It readily passes into the more stable grey metallic form; illumination by sunlight for a minute is sufficient to bring about the change, which is independent of the prevailing temperature. Yellow

[1] Kohlschütter, Frank and Ehlers, *Ann.*, 1913, 400, 268.

arsenic is vaporised even by the heat of the hand and, like the metallic variety, does not melt before subliming.

Antimony.—Arsenic and antimony are very similar in their allotropic forms, and what has been said above applies almost exactly to the modifications of antimony. The important forms are again a silvery brittle form crystallising in rhombohedra, and a light yellow form, which is not very soluble in carbon disulphide and cannot therefore be made by the method described for the preparation of yellow arsenic. It is formed when stibine is oxidised at low temperatures by a little chlorine or oxygen. The transformation into the stable form proceeds much more rapidly than in arsenic. When stibine is oxidised at 0° or allowed to decompose spontaneously a black form of the element is obtained which is identical with that produced when the yellow variety is exposed to light; it is so finely divided that it catches fire on exposure to air, but if heated in a non-oxidising atmosphere it becomes metallic in appearance, probably owing to an increase in the size of the particles. It is a more highly disperse form of the metallic variety.

The *explosive antimony* discovered by Gore, and more recently investigated in detail by Cohen and Ringer,[1] is produced by the electrolysis of hydrochloric acid solutions of antimony trichloride and forms a silvery incrustation which even when thick shows no indication of crystalline structure. When jarred, scratched or heated it is instantaneously converted into matt-grey masses with evolution of heat, but it can be pulverised without decomposition under cold water. A large quantity of antimony chloride is included in the deposit— up to 11 per cent.—and is set free as a cloud of smoke when the explosive decomposition takes place. This impurity varies in quantity with the concentration of the electrolyte, but when the antimony is explosive there is never less than 3 per cent. present. This effect is not, however, due to the liberation of the trichloride, for if a slow transformation is brought about, the salt remains enclosed in the stable form. It cannot be extracted from the powdered metal by solvents, so that it is not mechanically enclosed. It actually forms a solid solution with the unstable form of antimony. A similar solid solution of phosphorus can be obtained.

Phosphorus.—There are two fundamental modifications of phosphorus with other transitional forms. White (yellow) phosphorus and violet (metallic, Hittorf's) phosphorus are the chief forms. The violet form is the stable one under ordinary conditions, and white phosphorus is metastable and is only produced from the vapour of the violet modification. At 200° and 12,000 atm. or at room temperature and 35,000 atm. phosphorus is converted into a black graphitic mass which is not combustible, and which is denser than ordinary phosphorus.[2]

[1] *Z. physikal. Chem.*, 1904. **47**, 22.
Bridgman, *Engin. Min. Journ.*, 1921, **112**, 535 ; *Physical Rev.*, 1934, 45, 844.

The crystal structure of the yellow, red and black forms has been determined[1] and in each of them the P atoms are in groups of 4.

White Phosphorus.—As phosphorus is manufactured by the application of high temperatures, this form of phosphorus was the only one known for a long time, as it is produced when the vapour is condensed. It is almost colourless, with a slight yellow tinge, and when slowly solidified is almost transparent, particularly when sublimed or recrystallised from benzene. It forms well-shaped crystals when deposited from solvents; they develop a great number of faces and when sublimed *in vacuo* show all the forms of the regular system, except that with forty-eight faces. The brittle mass obtained when phosphorus solidifies from the fused state shows a crystalline fracture; crystallisation takes place very rapidly, frequently after a period of undercooling, since the heat of fusion of the element is very low—only 0·16 Cal. per g. atom.

White phosphorus hardly dissolves in water, but goes into solution without change in liquid ammonia, sulphur dioxide or cyanogen, as well as in the trihalide compounds of phosphorus; it is remarkably soluble in carbon disulphide, which is miscible with phosphorus in all proportions. A liquid mixture is described with 20 parts of phosphorus to 1 part of carbon disulphide. Many organic compounds serve as solvents, *e.g.* hydrocarbons, alcohol, ether, fatty oils and especially methylene iodide. The boiling point of white phosphorus at atmospheric pressure is 290°, but it vaporises even below its melting point. Its molecular weight is found to correspond to P_4 in all solvents.

White phosphorus ionises air which is passed over it—the air when led into supersaturated water vapour gives a mist. The oxygen becomes simultaneously oxidised to ozone, the reaction of each phosphorus atom converting 9·6 oxygen atoms into the active form. The appearance of ionisation is accompanied by a characteristic bluish light, which, as it is observed most intensely with phosphorus itself, is called phosphorescence. The precise relations between the phosphorus, the ionisation of air, the luminosity phenomenon and ozone formation are not quite clear. Actively oxidising bodies do not always ionise gases, nor is phosphorescence a usual accompaniment of oxidation reactions. The production of light is a form of transformation of chemical energy; as in some reactions it is set free in the form of heat, so it appears in the form of light vibrations in the phenomenon of phosphorescence. The effect is called chemiluminescence. It is not the solid phosphorus but its vapour which is seen in the dark; a stick of phosphorus is seen to be surrounded by a luminous haze, which is whirled in clouds about the stick. When ozone appears in the oxidation of phosphorus, free oxygen atoms are

[1] Hultgren, Gingrich and Warren, *J. Chem. Physics*, 1935, 3, 351 ; Thomas and Gingrich, *Ibid.*, 1938, 6, 659.

also formed, so that it is possible that the light is not actually due to phosphorus, but is a similar phenomenon to the yellow afterglow of nitrogen (cf. p. 114).

The luminosity depends on the temperature, and it is extinguished in the cold. It is also dependent upon the presence of oxygen; very small quantities of oxygen produce it, and larger quantities increase the effect; but in apparent contradiction to the law of mass action and in an extremely striking manner, the maximum illuminating power is obtained with a certain oxygen pressure, but at a still higher pressure it disappears altogether. The speed of oxidation changes parallel with this, and in pure oxygen at a pressure of 700 mm. or more it is zero; on diminishing the pressure it increases, and at approximately 300 mm. it reaches a maximum; an additional decrease of pressure causes a diminution. These data, at room temperature, do not alter much with the temperature, the maximum illumination (and oxidation) at 0° is at 320 mm., and the optimum pressure increases by 13.19 mm. per degree of temperature. The presence or absence of water has a great effect; in completely dry oxygen a state of luminosity and oxidation is obtained only at a pressure of several atmospheres. Many other bodies such as iodine, sulphuretted hydrogen and turpentine negatively catalyse the reaction, and the velocity is reduced so effectively that both oxidation and light emission cease practically completely when a very small amount of them is present.

According to Weiser and Garrison,[1] the luminosity is not due to the oxidation of the phosphorus itself, but to the subsequent conversion of the trioxide to the pentoxide. They suggest that continuous oxidation takes place only when the rate of evaporation of the phosphorus is greater than the rate of reaction with oxygen; otherwise the oxide is deposited on the surface of the phosphorus and the vaporisation thereby prevented. Arsenic also phosphoresces between 250° and 300°, if the pressure is suitably low, and the glow is due to As_2O_3.

According to the observations of N. Semenov and G. Rjadbinin,[2] there is a lower and upper limit to the oxygen pressure in the combustion of sulphur, within which limit only does oxidation take place; this throws some doubt on the theory of a solid sheath as none can be formed with sulphur.

Phosphorus precipitates metals from solutions of their salts (cf. p. 203) and even takes up positive charges itself, a property paralleled by no other non-metal.

Violet Phosphorus.—The violet form of phosphorus, also called the metallic, is most easily prepared by Hittorf's method of allowing phosphorus to crystallise from molten lead. It can be obtained to a smaller extent from melted bismuth.

[1] *J. Phys. Chem.*, 1921, **25**, 61, 369, 473; cf. *Nature*, 1925, **115**, 460; *J. Chem. Soc.*, 1925, 127, 1362.   [2] *Z. physikal. Chem.*, 1928, B1, 192.

It is formed in small leaflets, curved like tulip petals, which are monoclinic and transparent, exhibiting a steely-blue metallic lustre. Only a little phosphorus dissolves in the lead, so it is very difficult to obtain any quantity from the mixture. The lead must be dissolved out by nitric acid, and the acid also attacks the phosphorus. Better results are obtained if the lead is removed electrolytically.[1] A product very similar to Hittorf's phosphorus in colour, density, optical and other properties, but not very pure, is obtained by the systematic levigation of commercial red phosphorus with water. The heavier particles are left behind as dark, steely-blue leaflets and scales which resemble iodine in appearance.

Violet phosphorus is insoluble in all ordinary solvents; it does not phosphoresce in air or in a current of steam. Chemically it is very much more inert than the white variety. It ignites at 260° and only oxidises on prolonged exposure to the air. Its melting point is indefinite but lies round about 600°. Its vapour pressure is markedly different from that of white phosphorus; at low temperatures it is less, and it is actually possible to sublime violet phosphorus *in vacuo* at 100°, so that at that temperature there is a difference between the forms of phosphorus even in the state of vapour. At higher temperatures the vapour pressure of the violet form approaches that of the white and ultimately exceeds it. It then behaves like a monotropic modification. When chilled in this condition it yields no red phosphorus but only white. On the other hand, the vapour pressure of violet phosphorus mixed with a little white phosphorus sinks in time; the white vaporises first, is then deposited in the red form, and so gradually disappears. The drop in pressure takes place, though not abruptly, with the disappearance of the last portions of white phosphorus; for the latter gradually forms a solid solution with the violet phosphorus, the vapour pressure of which becomes lower as its content of white phosphorus becomes less.

The molecular weight of violet phosphorus cannot be determined because it dissolves in no solvents and when rapidly vaporised is quickly converted into yellow phosphorus. Hence it is not known for certain whether the difference between the forms depends on an increase in size of the molecules of the white phosphorus (polymerism), or whether with an equal number of atoms in its molecule the arrangement of atoms in the crystal is different (polymorphism). The first assumption is the more probable since the inoculation of the solutions or melts of white phosphorus with the metallic variety causes no additional crystallisation of the latter to take place, although it is the more difficultly soluble. In a case of polymorphism the violet form should be produced. Black phosphorus is converted into the violet form by heating to 125° especially with a little iodine.

Red Phosphorus was first prepared by v. Schrötter in 1845 and is

[1] Stock and Gomolka, *Ber.*, 1909, 42, 4510.

made by heating white phosphorus with exclusion of air to a high temperature. It is also formed when the solutions of the white modification are exposed to light. Red phosphorus is not a definite product. Very probably it differs from Hittorf's phosphorus in the size and arrangement of its particles, which has been disturbed without complete disorientation. This form possesses glassy properties but slowly devitrifies and becomes crystalline. The degree of disorientation of the molecule varies with the temperature of preparation and, even in individual samples from the same batch, portions can be picked out which are very closely related to Hittorf's phosphorus. The failure to form crystals of the latter depends upon the formation of solid solutions with the solvent; it is contaminated and its tendency to crystallisation is reduced. It takes up considerable quantities of carbon disulphide and is precipitated from phosphorus tribromide with an irremovable content of 30 per cent. PBr_3. Even white phosphorus itself is enclosed when the red is made by the transformation of the fused allotrope, though it does not exhibit its original properties, being in a solid solution. On prolonged heating the white phosphorus becomes transformed to a large extent into violet, so that the red gradually becomes more like the violet.

Conversely, the white form is produced from the violet, so that a pure violet form cannot be obtained. There is probably an equilibrium between the two forms dependent on temperature. In fact, the density of the product varies with the temperature of preparation. According to Cohen,[1] the allotropes of phosphorus are dynamic and not monotropic.

Even with an equal percentage content of violet phosphorus in the white, different products are obtained with quite dissimilar properties. The colour, for instance, changes very remarkably according to the proportions of the mixture, but is chiefly dependent upon the dispersity of the violet phosphorus. Large dark crystals of all kinds of materials become lighter when powdered, as small particles of the mass reflect white light instead of absorbing definite wave-lengths. So it is probable that in larger crystals of the iodine-like forms of phosphorus the colour varies according to the dispersity, from violet or deep red to light scarlet or orange red. Optically, red phosphorus is completely isotropic, showing no internal orientation; the darker it is the greater its action on polarised light.

The lightest red phosphorus is obtained by exposing a solution of white phosphorus in carbon disulphide to light, or in greater quantity by boiling a 10 per cent. solution of white phosphorus in phosphorus tribromide for some hours.[2] When it is prepared in the latter way a great deal of the solvent remains in solid solution; it can be made almost free from it by reducing phosphorus tribromide with metallic

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[1] *Z. physikal. Chem.*, 1910, **71**, 1.
[2] Schenk, *Ber.*, 1902, **35**, 351; 1903, **36**, 980.

mercury under pressure, first at 100° and later at 170,° and extracting the remaining impurities (PBr_3 and $HgBr_2$) with ether. The phosphorus tribromide acts as an accelerator. The transformation of phosphorus by heat, which is explosive at a high temperature, is slow enough to be studied at 310°; the velocity of transformation is strongly affected by catalysts, which accelerate the transformation by both light and heat. Besides selenium and phosphorus tribromide, phosphorus tri-iodide is very effective; the reaction takes place even at its melting point and considerable heat is evolved. Similar spontaneous evolution of heat takes place when white phosphorus is heated to about 300°, when the temperature may go up by as much as 100°.

The lighter the colour of the phosphorus the more active it is. This is due not so much to its content of white phosphorus, of which very little can be extracted by solvents, but to the fine dispersity of the particles giving a greatly increased surface. Although light red phosphorus is totally non-poisonous and does not catch fire in the air, it still has the property of dissolving in alkalis. Like white phosphorus, it evolves heat on conversion to a darker form, but this may be due merely to the reduction in surface when small particles combine to form larger ones.

Boron and Silicon.—Both these elements exist as an amorphous powder and as a crystalline modification, but the identity of the crystal lattice proves that the molecular form is not different. Apparently amorphous forms always appear where a closer union of the smaller particles is not possible, whereas crystals are formed when the element is produced by solution or distillation. When nascent boron and silicon are formed by reduction in a medium which is not a solvent for them, they appear in the amorphous state. To obtain the crystalline forms it is necessary to employ a large excess of a reducing agent, preferably one such as aluminium, which is a pronounced solvent for these elements. Crystals are also obtained by recrystallising or distilling the amorphous forms. The crystalline and amorphous forms do not differ more in their general properties than might be expected from the mere difference in the size of the particles; e.g. the densities (2·35 for amorphous, 2·48 for crystalline) are of the same order of magnitude. X-ray analysis yields results which indicate that these are only secondary modifications in both cases. The separation of a slightly volatile and insoluble body, out of a medium in which its mother substance was distributed, does not produce crystals, because the primary particles formed cannot orientate themselves, as they are isolated by the medium. They are first formed in a molecular state of subdivision from the gaseous condition and only have a very slight orientation to each other, when they are deposited on the surface in the form of dust. Even here they are in or near the molecular state of the gaseous condition, and Kohlschütter has indicated

this state of aggregation of the material very appropriately as the "pseudo-gas" state. The pseudo-gas molecules return again to free mobility while they are dissolved in a solvent, so that they can then be deposited in the solid condition in the crystalline form.

The amorphous forms conduct an electric current badly, while the crystalline forms conduct like graphite. It has been demonstrated that even a coating of condensed metal does not conduct a current.

Amorphous silicon is dark brown, becoming lighter on ignition, and amorphous boron is grey brown to dark greenish brown; crystalline silicon is brown and transparent in thin sheets; and a crystalline boron which is a red-brown glass has been described. Both elements form octahedral crystals; boron also forms tables and prisms. The crystals of silicon are dark iron black, but the boron crystals are described in very varying forms, some as metallic shining black leaflets, others as colourless crystals with a bright diamond lustre. Pure crystalline boron is not known at all, and both forms (like phosphorus) contain large quantities of the crystallising medium; in fact, the dark form may be an aluminium boride AlB_{12}, and the analysis of the diamond-like form gives the formula $Al_3C_2B_{48}$. It is obvious that both these forms stand in very near relationship to each other, and this is further demonstrated by the extraordinary hardness of both. They are as hard as diamonds, or even harder.

Silicon melts in the electric furnace and then vaporises, while boron is not fusible but only sublimes. It is distinguished by its low atomic heat (3·4), which increases rapidly with rise of temperature, and at 400° has attained the normal value of 6·4. It resembles in this its neighbour in the Periodic Table—carbon.

Carbon

Carbon exists in many forms, but only three can be definitely characterised—the diamond, graphite, and "black carbon." The vitreous carbon found in retort carbon is allied to graphite, while all the forms of active carbon belong to the third class. Only the diamond and graphite exist in a completely pure form, for the varieties of black carbon usually contain admixtures of graphitic material, while vitreous carbon not only contains graphite but, according to its method of formation, may approach the diamond in properties. Graphite has varied properties depending on its structure, as shown by the radiograms of the latter, and many varieties were formerly distinguished. Black or amorphous carbon has an even greater number of sub-varieties. The X-ray analysis of these forms gives a closer insight into their real structure than any other method; the difference between diamond and graphite is shown on p. 21, and what is known of the structure of the other types of carbon will be indicated below.

The relative stability of these forms is only known on general grounds; it is probable that the diamond is in the metastable condition

at low pressures and at all temperatures, whereas black carbon or graphite is the stable modification. The heat of combustion, the best measure of the relative energy content, is very similar for diamond and graphite; for the diamond it is 7873 calories per gram, while for one kind of graphite it is 7832 calories per gram. Graphite thus only differs to an insignificant extent from the diamond in this property. The difference is not altered at high temperatures, but from 100° upwards a very slow transformation of the diamond into graphite is observed, which proceeds rapidly at very high temperatures.

Carbon vapour obtained by electrical heating condenses as graphite, and fine crystals often appear with the shape ascribed to a benzene ring. The transformation of graphite into diamond has never been observed. Graphite is specifically lighter than the diamond, and if graphite were strongly compressed until the volume of the diamond was reached, a spontaneous transformation would be possible; but the density of the diamond is 50 per cent. greater than that of graphite, so that an enormous pressure would be required. As the compressibility of diamond is not known, the point of transformation cannot be determined.[1]

Diamond.—Diamonds have, however, been made in experiments at very high temperatures. Moissan obtained a high pressure by making use of the fact that iron saturated with carbon expands on cooling, whereas iron containing little carbon (wrought iron) contracts. A wrought-iron cylinder which was completely filled with charcoal was heated in a bath of molten iron till melted and then cooled by plunging the mass into water. Thus the iron rich in carbon was inside the mass, and that poorer in carbon in the outer layers; the latter contracted on cooling, and compressed the expanding inner layers. The yield was in fact very small—partly white and partly black transparent diamond crystals. They were isolated by the solution of the iron in acid, treating the residues with oxidising agents (HNO_3, $KClO_3$) to dissolve out the black carbon and finally with hydrofluoric acid to remove other impurities. The total yield of fifty operations was only ten milligrams. Better results were obtained when molten pig-iron, saturated with carbon, was allowed to drop into water. The solution of carbon in metals other than iron, *e.g.* in silver, gave even less satisfactory yields. The diamond is known to occur in nature in silicate rocks, so these were tried as solvents for carbon; but they dissolve only very small quantities of carbon, though on cooling it crystallises without application of pressure as diamonds. According to Ostwald's Law the more unstable modification is formed first, so that this method of preparation on the whole is not without promise, though the diamond and graphite differ but little in stability. It is very probable that the carbon first appears in the metastable form, but that it only remains in this state if the temperature is rapidly

[1] Roth, *Z. Elektrochem.*, 1915, **21**, 1.

reduced. The extreme minuteness of the diamonds so produced makes it doubtful whether the formation in nature goes on in a like manner, for diamonds have been found with weight up to 630 g. There is no doubt from the crystal structure that they are formed from the fused mass, and not by the transformation of previously formed graphite. Diamonds are invariably of the regular system, though the actual crystal shape varies in different localities. Brazilian diamonds exhibit the cubic form, but the South African ones are usually octahedra or hexakisoctahedra, the others being apparently holohedral. The inclusions in diamonds are interesting and important as indicating their mode of formation. Many contain small crystals of iron pyrites or of black carbon. Carbonado is black diamond found in pieces up to one kilogram in weight, which shows very slight contamination, but on account of its coloration it has no importance as a gem but is used as an abrasive, like black boron crystals (p. 136). Its properties are otherwise those of the clear diamond. Blue, red or green diamonds are especially valuable, though when the stone shows a slight yellow coloration its value as an ornament is reduced. The native diamonds often contain smaller included diamonds, which, on account of the different refractive powers of some of them, shine like bright spots. Even red diamonds are sometimes included inside the colourless ones. One of the most frequent defects in diamonds is the existence of a hollow space, which is sometimes fairly large.

The diamond surpasses nearly all other bodies in hardness and refractive index ; its high price is due to its rarity and its immunity from chemical influence. The extreme nature of its properties makes it one of the most interesting substances from a chemical point of view. Thus at ordinary temperatures it has the least atomic heat of all elements, namely, 1·25, instead of Dulong and Petit's average figure, 6·4. On raising the temperature the atomic heat increases rapidly as in other substances, and reaches the value 5·5 at 985°. At $-186°$ the atomic heat amounts to only 0·03, and at $-227°$ it is almost nil; that is, the diamond in an enclosure at $-273°$ shows the same heat content as in an enclosure at $-227°$. The warming of the diamond from $-273°$ to $-227°$ is effected without measurable addition of energy. The accuracy of Nernst's hypothesis that the specific heat of bodies is lowered to zero with decreasing temperature is more easily demonstrated with diamond than with any other substance.

Robertson, Fox and Martin[1] discovered that diamonds exist also in a laminar form, which is rare, but has several properties different from those of ordinary diamonds. Both forms show a cubic structure, but the laminar form, as its name indicates, has also fine parallel laminations. The infra-red absorption spectrum of ordinary diamond shows a band at $8\,\mu$, which is absent from the spectrum of

[1] *Phil. Trans.*, 1934 [A], 232, 413.

the laminar variety; the former is opaque to ultra-violet light at 3000 Å, the latter at 2250 Å; and whereas the photoelectric conductivity of ordinary diamond is small that of laminar is considerable; further, ordinary diamond is less optically isotropic than laminar diamond. The refractive indices, specific gravities, dielectric constants and Raman spectra of each are identical. The differences are considered to arise from differences in the conditions of production from the plastic state, and not to be due to impurities.

Vitreous Carbon.—This form of carbon is a graphite which approaches the diamond in properties.[1] It is formed by the decomposition of gases containing hydrocarbons at smooth surfaces at a temperature above 650°. The material of the surface must not be capable of forming a carbide, and porcelain, quartz, fluorspar, carborundum, diamond or gold can be used. The formation of free carbon in the gas itself must be reduced to a minimum, otherwise only soot is produced. The formation of the vitreous carbon depends entirely on the fact that it is produced on a surface—it is a topochemical process. One method is to direct a cold stream of the gas against a hot glazed porcelain crucible, when the vitreous carbon is soon apparent from its high metallic lustre like that of platinum. In contrast with graphite, it is glassy, hard, elastic and very resistant to chemical attack. For instance, it does not dissolve if heated with concentrated sulphuric acid and mercuric sulphate, or with nitro-sulphuric acid, or if fused with sodium sulphate, processes which all rapidly attack graphite. The hardness of this form of carbon is remarkable; when prepared at 1800° it will even scratch corundum. It is therefore not surprising that the X-ray analysis of this material shows that the graphite lattice has suffered a deformation in the direction of that of the diamond. The valencies of the carbon atoms are not, however, quite equal, and one is weaker than the other three. The electrical conductivity of the vitreous carbon, again, is more analogous to that of the diamond, for it is only one-eighth that of graphite.

Vitreous carbon is very variable in its properties, which depend, for example, on the temperature of preparation. The higher the temperature the larger the crystals; thus ordinary vitreous carbon made at low temperatures consists of small crystallites; retort carbon with its higher temperature of formation contains coarser crystals; while graphite, formed at a very high temperature, consists of macroscopic crystals. According to U. Hofmann,[2] these three are not really different forms of carbon, but their varied properties, such as hardness, appearance and chemical resistance, are due to the disposition of the small crystallites and their increased size at high temperatures. Thus

[1] K. A. Hofmann, C. Röchling and U. Hofmann, *Ber.*, 1923, 56, 2071; 1926, 59, 2433.

[2] *Ber.*, 1928, 61, 1180.

vitreous carbon would be considered only as a sub-variety of one of the allotropes of carbon; but the mechanical differences in these modifications of graphite produce such great differences in chemical and physical properties that, even if they are due to differences in the secondary structure only, they are just as great as those caused by a change in the primary form.

Graphite and Black Carbon.—It has recently been much discussed whether these two forms of carbon are really distinct.[1] Debye and Scherrer, as a result of X-ray examination of the crystal structure of various forms of carbon, have come to the conclusion that the black form is only graphite reduced to a crystal size beyond that which is possible by mechanical means, so that there are really only two forms of carbon—diamond and graphite.

Kohlschütter[2] demonstrated that all kinds of intermediate stages between amorphous carbon and graphite can exist. O. Ruff,[3] on the other hand, claimed that there is really a fundamental difference between the two classes, but that each is capable of wide variations in the arrangement of its primary particles, so that a continuity of properties is observed. Soot, wood charcoal, retort carbon and other similar substances were formerly classified as amorphous carbon, but without accurate definition of the varieties; while the graphite group was determined partly by appearance and partly on the basis of behaviour with chemical reagents, but the varieties overlapped. If mere appearance is to be taken as a guide, graphite and soot or wood charcoal seem different substances; for the first is almost metallic in appearance, while the others are dead black and devoid of lustre. Graphite is soft, cold and greasy to the touch, whereas charcoal is hard and brittle and has an irregular fracture in contrast to the flexible flakes of graphite. Charcoal is a bad conductor of electricity, whereas graphite conducts well. All these differences tend to show that the two substances are fundamentally different, but it must be remembered that these distinct properties are those of extreme forms. Even within the kinds grouped under these two forms there are gradations in properties which are not of an order to be ignored. Thus charcoal has different densities when prepared at different temperatures or from different materials. Wood charcoal is the lightest, and varies in density from 1·45 to 1·55; soot from hydrocarbon oils and sugar charcoal varies between 1·72 and 1·79, while soot from acetylene and some graphitic gas carbons has a density between 1·9 and 2·0. The ignition temperature of wood charcoal prepared at a low temperature is about 300°; soot ignites at 371°, but if heated for a short time to 910° it ignites only at 440°, and heating to the same temperature for three

[1] *Cf.* Riley, *Chem. and Ind.,* 1939, **58**, 391.
[2] *Z. anorg. Chem.,* 1918, **105**, 35.
[3] *Kolloid-Z.,* 1926, **38**, 174; *Z. anorg. Chem.,* 1926, **148**, 313.

hours raises the ignition point to 476°. The electrical conductivity always depends on the thermal history of the sample.

The same variation in properties is found in the graphites: the hardness varies between 0·5 and 2·0; the density from 1·8 to 2·34, the coefficient of expansion from 0·55 × 10^{-7} to 24·4 × 10^{-7}, and the specific conductivity from 0·054 to 0·247. These properties are also affected by heat treatment, but on cooling again they tend to return to the original values. The low value for the hardness of graphite depends on the fact that in the ordinary test only the fourth and weakest valency of the carbon atoms comes into play, that is parallel to the cleavage planes. At right angles to these planes its hardness approaches that of the diamond. The effect of various reagents on different samples of graphite is also variable: some kinds, on soaking in nitric acid and then heating with it, swell up into voluminous vermiform masses, while other samples show this effect in a much less marked manner, and others not at all. The difference in the effect of nitric acid is so marked that the graphites were for a long time subdivided into the graphites and the graphitites—the latter being those which did not swell on treatment with this reagent. The action of oxidising mixtures such as chlorates and nitric acid also varies with different graphites. Some (like diamond) are not attacked at all, others dissolve very slowly, while some are rapidly oxidised to yellow substances which contain oxygen and hydrogen as well as carbon and are known as graphitic acids.

The differences in properties are paralleled by the differences in outward appearance. In the graphites, black dull varieties are known, as well as the commoner form of large greasy metallic leaflets with a metallic streak. The former give hard lumps like coke or anthracite on washing, and even in the latter there are granules and cores, as well as minute crystals and very small particles dispersed throughout the rocky matrix in an almost amorphous form. Artificial Acheson graphite (p. 180) contains all the various forms side by side. It is thus clear that the name graphite covers a number of different substances.

The great variety in the black forms of carbon becomes slightly less confusing if we regard the forms as derived from ideal amorphous and graphitic forms. The results of the study of the X-ray structure are explained by the idea that there really is a continuous series as far as the arrangement of the atoms in the layers is concerned, but with different dispositions of the layers. According to Kohlschütter's view the formation of graphite takes place only at surfaces, and the flatter the surface the more like graphite the product, while when the surface is roughened non-graphitic forms are produced. The place of formation thus determines the nature of the product (topochemical formation). When carbon is deposited inside a three-dimensional

medium the particles cannot then arrange themselves in a definite design, but only grow by a kind of adsorption process. This takes place, for example, in the formation of soot in the air; the air is adsorbed on to the primary particles and separates them in the mass finally formed. The charring of carbohydrates by heat or by concentrated sulphuric acid does not provide any better facilities for definite arrangement.

If illuminating gas is decomposed at a red-hot glazed porcelain surface, a hard deposit of carbon similar to retort carbon is obtained; if, however, the surface is unglazed, the deposit is more powdery, though still graphitic. Again, acetylene decomposes with deposition of carbon at 800°, but if it is passed through a copper tube heated only to 400° it suffers decomposition, but only at the surface of the metal and not in the bulk of the gas. The carbon is deposited in a graphitic form. The equilibrium $2CO \rightleftharpoons C + CO_2$ is disturbed by the presence of iron in favour of the deposition of carbon, which then takes place at as low a temperature as 300°. The deposited carbon may be either graphitic or sooty, according to the dispersity of the iron. Molten iron, as is well known, dissolves carbon, which it partly deposits on cooling in the form of graphite. It is probable that when the iron contains less than 4.27 per cent. of carbon, crystals of iron carbide Fe_3C (cementite) separate out first and give the graphite on decomposition; this proceeds layer by layer in the cementite, and thus the deposition takes place on the crystal faces, and pseudomorphs of cementite in graphite are produced. The formation of Acheson graphite appears to be due to a similar phenomenon—the silicon carbide crystals decompose layer by layer so that the carbon is left in the graphitic form.

The structure of graphite has been confirmed by X-ray analysis (cf. p. 21). The distance between layers is greater than that between atoms in the same layer, and on the application of pressure the layers can be forced closer together, while the atoms in a given layer are scarcely affected. This arrangement of the atoms gives rise to the laminated structure of graphite; and the spaces between the layers of atoms permit the easy passage of gases through the solid and account for the adsorbing power of graphite. The intumescence which is observed when graphite is heated with nitric acid is also a consequence of this structure, for the acid penetrates between the laminæ, and the products of the reaction separate layer from layer and thus cause the whole mass to swell (see also p. 776). The swelling, indeed, depends on the extent to which the carbon is laminated in structure (cf. swelling in substances like bentonite, montmorrilonite, etc.). The stratifications persist in the oxidation products of graphite; the graphitic acid formed on treating with nitric acid and potassium chlorate retains the shape of the graphite from which it originates, and if carefully

decomposed is reconverted into a similar mass of carbon. The graphitic acid is yellow to greenish in colour, and if heated rapidly gives sooty clouds on decomposition.

The chemical activity of the forms of carbon is naturally dependent on the structure of the various allotropes. The more loosely packed forms are more readily attacked by reagents, owing to the larger surface they present; they also adsorb gases more readily and are more easily ignited, just as finely divided metals burn more easily than the same substance in massive pieces. The greater heat of combustion of the loose packed varieties can also be explained, for reduction in surface always gives rise to evolution of heat, as can be observed in the coagulation of aqueous colloids. It can easily be understood that the specific heat of the graphitic forms of carbon and of the various forms of coke is the same, although their chemical behaviour may be different.

The most important form of black carbon is *activated carbon* (Ruff). This product is made by heating inactive carbon in steam, carbon dioxide, ammonia gas, sulphur dioxide, and even air. It differs from inactive carbon in having a very much greater capacity for adsorbing dissolved substances, *e.g.* phenols, which is also greater than its power of adsorbing gases. As Ruff has shown, the properties of the amorphous forms of carbon are greatly affected by the fact that the particles, composed of amorphous material, are enclosed in a graphitic skin, and activation consists in the removal of this layer. The differences in density between samples of black carbon depend not only on the admixture of graphitic material in the mass of the particles but more on the thickness of this shell of graphite, which prevents the access of liquids to the more diffuse carbon in the interior. When investigated by the X-ray method black carbon shows a more or less definite interference diagram of the graphite type. This is more developed when the carbon is heated, most completely when the heating takes place at a high temperature.   According to Berl,[1] in active carbon the three-dimensional lattice of the graphite is broken down into a two-dimensional one, and further, presents those irregular points on which the adsorptive power depends.

Amorphous carbon can thus be converted into graphite, and an intermediate form has been isolated. This form cannot be activated and on the other hand gives such a feeble indication of graphite in its crystal structure that it cannot be classified as a graphite. Ruff suggests that in this a rearrangement of the carbon atoms has begun, but that the graphite lattice has not been completely developed. Many wood charcoals are of this type, with the carbon atoms arranged, it is true, in lamellæ, but the latter are three atoms thick. No definite crystal lattice is apparent because the lamellæ are crumpled up. This arrangement of particles may be compared to a solidified foam and has been

called paracrystalline. These thin lamellæ cause the carbon to be more active than graphite chemically but increase the electrical resistance. When the outer original layer is thick, the hardness and to a lesser extent the density of the carbon are greater and graphitisation takes place more readily.

Metals

Many metals have numerous modifications which show enantiotropic relations to one another. This general property was first emphasised by Cohen,[1] for it had been overlooked up to that time owing to the retardation which most of the transformations suffer, so that their true nature is not obvious. Cohen was able to demonstrate that practically all metallic forms, including alloys, were in a metastable condition at the ordinary temperature. It is only necessary to give a start to the change and the whole mass of metal is rapidly converted to the stable form. The origin of his work was an investigation of "*tin pest.*" Objects made of tin sometimes show blistery outbreaks on their surface, which gradually spread until the whole surface becomes brittle and when touched falls to a sandy powder. The effect was first noticed in the organ pipes in unheated churches and in tin objects in museums; whole piles of tin ingots were sometimes affected, and on one occasion a large delivery of tin uniform buttons was reduced in one day to a formless mass. The tin resulting from the change is grey in colour and entirely lacks the metallic lustre of ordinary tin.

The grey tin was shown to be an enantiotropic form of the metal by the observation that when it was heated with hot water it regained its original lustre, and its volume, which is greater than that of the white tin from which it is produced, was altered to its original value. White tin, on the other hand, can be deliberately converted into the grey variety if it is infected with it at low temperatures. The transition point can be detected dilatometrically and lies at 18°-20°. A mixture of the two kinds of tin neither contracts nor expands at this temperature, while at higher temperatures a contraction is observed and an expansion takes place on cooling, due to the disappearance of the grey tin on heating and of the white tin on cooling. The same transition point is found if electrodes of grey and white tin are placed in a solution of a tin salt and the resulting potential difference followed. At about 20° this is zero, but below this temperature white tin, and above it the grey variety, has the greater solution pressure. As the ordinary temperature in temperate climates is usually below 20° it follows that all tin is in the metastable condition except on a few very warm days; and it is only because the rate of transformation is so slow that the tin remains unaltered on most occasions. This pseudo-stability disappears at once

[1] *Z. physikal. Chem.*, 1899, 30 ff.

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if the tin is placed in a solution of a tin salt. The deposition of tin takes place owing to the small currents set up by differences in concentration in the solution, and the tin is naturally deposited in the form stable at the temperature of the experiment. The small amount of grey tin which thus separates out at temperatures below 18° is enough to infect the whole mass of tin. The rate of transformation is thus markedly affected by the presence of tin salts, and whereas dry tin shows a maximum rate of change at −48°, when immersed in a solution of a tin salt the change is most rapid at 0°.

The previous history of the tin also affects the rate of transformation, and a sample which has been undercooled for a long time is converted into the grey form much more rapidly than tin which has not undergone this treatment. Again, if some grey tin is transformed into white and then back again into grey, the second change takes place more quickly than with fresh tin, and the more often the tin has been transformed the more rapidly the change takes place. Even the transition temperature is affected by a repetition of experiments or by intermediate heat treatment; with cadmium it can be depressed from 70° to 62°.

Similar changes are shown by many metals and possibly by all, but the detection of transition points is difficult, owing to the effect of undercooling and of superheating. The change at the true transition point takes place very slowly indeed. Metals are mostly obtained by the solidification of fused masses, so that the crystals obtained in this way are metastable at room temperature and are subject to a slow change to the stable form. Their properties thus depend to some extent on their age and the mechanical and heat treatment they have undergone. The very divergent data for the physical properties of the metals are due to the fact that the materials studied are often in a partly transformed state. Records of density, hardness and almost all physical properties, with the exception of atomic weight, are of little value unless the method of preparation and form of the metal is carefully recorded. Cohen has shown that even the specific heat of metals is dependent on their thermal history.

The existence of definite allotropic modifications has been demonstrated in copper, thallium, cadmium, aluminium, lead, antimony, and even in sodium. The phenomenon has not yet been observed in mercury. Alloys also show the tendency to undergo these changes, and the ordinary forms are usually metastable. German silver wire reverts to the stable form when kept for a long time and becomes brittle, while brass vessels in daily use often show the effects of considerable decomposition.

The effect of temperature on the brittleness of metals has been known for a long time. Zinc, for example, is not easily filed at the ordinary temperature, and attains a maximum malleability and ductility at

100°-150°, though at 250° it again becomes so brittle that it can be powdered in a mortar. The brittle form can be preserved at the ordinary temperature if molten zinc is rubbed up with an iron pestle till solidified, or cooled with some rapidity. In the same way the normally ductile metal tin becomes brittle and easily broken at high temperatures when the tetragonal white tin passes into a white rhombic form. The transition point is uncertain; values between 161° and 200° have been reported by various workers. The three different forms of tin differ a good deal in their physical properties; for instance, their densities are: grey tin, 5·80; tetragonal (ordinary) tin, 7·29; rhombic tin, 6·55. Each of these changes is enantiotropic, the transition temperature grey $\longrightarrow$ tetragonal being 18°, and of tetragonal $\longrightarrow$ rhombic 161°; rhombic is stable up to the melting point (232°).

A similar transition point has been fixed for aluminium at 533°. Bismuth is ductile when freshly cast but becomes brittle on ageing. These examples might be multiplied to show how widespread this phenomenon is. Traces of impurities affect both the nature and temperature of transition.

Yet another kind of alteration in the properties of metals is produced by mechanical treatment. Cohen studied the effect in tin, and applied the term "strain disease" to the breaking down of the structure which can be observed. When the crystalline structure is upset by rolling, or its development restricted by a great extension of the surface, as in tin-foil or on tin-plate, recrystallisation (p. 149) can set in. The same result had been observed previously as a consequence of heat treatment over long periods. It indicates that the change is not enantiotropic, for there is no definite transition point. The heating only induces processes which can continue at much lower temperatures —even the inoculation with recrystallised tin is infectious. The change spreads much more rapidly than tin-pest, and if a few grains of recrystallised tin are placed on a piece of tin-foil or tinned iron the whole is transformed in a few days at room temperature. Tin which has been treated with acids acts as a germ for this change; e.g. tin moirée, obtained by treating block tin with a mixture of hydrochloric acid and potassium chlorate to make the crystalline structure visible to the naked eye. Tin-foil and tin-plate thus contain a form of tin which is different from rhombic, tetragonal and grey tin, and which is metastable to white tin above 19° and to grey tin below that temperature.

The behaviour of lead shows how careful one must be in classifying changes in metals as allotropy. If a stick of lead is placed in lead nitrate solution it rapidly breaks up to a fine crystalline powder. This change, however, is not affected by any transition temperature, and ceases at once when the lead is removed from the liquid. The powder is thus not a product etched from the solid, but a result of the chemical action of the solution. The effect is known as the "disglomeration"

of the crystallites of which the solid lead is made up.[1] Between the
crystallites are thin layers of eutectics with the traces of impurities of
the lead, and these dissolve more readily than the pure lead. A kind
of lead tree is thus formed in the solution——some of the lead going into
solution and some being deposited as a result of the potential difference
set up by the presence of pure and impure lead. These impurities are
not essential for the formation of the lead tree, as pure lead crystals
also give trees; they become surrounded with a thin layer of a basic
lead salt, within which the solution is weaker in lead ions than it is
outside, and the potential difference set up in this concentration cell
causes the deposition of the lead tree.

Some metals undergo alterations in form at high temperatures.
When the metal is magnetic the change is easily observed by the
change in this property, though the volume and the specific heat some-
times alter as well. Iron gives three such points, cobalt two, and nickel
only one :

Fe	Co	Ni
770° 890° 1410°	444° 1150°	350°

Ordinary zinc shows a sudden alteration of properties at 304° and
thallium at 225·2°.

Structure and Mechanical Properties of Metals.—It has been mentioned above
that the mechanical properties of lead can be altered without the appearance of a
new allotropic modification of the metal. The hardness, ductility and toughness of
many metals can be altered in a desired manner by heat treatment or cold working,
which produce the effects summarised in this paragraph. If a polished section of
metal which has been treated with an etching reagent is examined under the
microscope, single crystallites will be observed which, on account of their boundary
lines, are clearly defined and give the whole section a honeycomb appearance.
These lines do not represent the edges of crystals, but are produced during the
solidification of the melted metal, when centres of crystallisation are formed in
different places, from which solidification takes place in all directions. If two of
these zones of crystallisation increase equally in the same plane they will eventually
meet, and at this point their progress will be interrupted, but can continue in other
directions until contact with another circle occurs ; this continues until the contact
points form a line which represents the limits of crystallisation. The pattern is
made visible by etching because the impurities in the metal separate last from the
fused mass ; the particles most recently solidified are those on the boundary lines
of the crystallites, and corrosion has a different effect on these particles from that
on the pure metal.

As the metal masses are not homogeneous it is possible to alter their properties
by mechanical means ; thus the gaps between the crystals can be partially closed by
forging, rolling, drawing, etc., whereby another alteration often takes place, i.e. the
formation of slip planes. The latter, in consequence of their structure, are clearly
visible under the microscope, and occur within individual crystallites, causing their
deformation and determining their ductility. In deformation each crystal splits up
into a variable number of thin lamellæ, which adhere together but are nevertheless
distinct from one another. The greater the number of slip planes the more readily

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can the crystal be deformed. In the most ductile metals (gold and copper) the appearance of slip planes in the crystallites is seen to occur before the individual crystallites are displaced. In the less ductile metals (silver) the formation of slip planes coincides with the forcing together of the crystallites ; and it is easier to push the crystallites together in this manner in the harder metals (iron, nickel, magnesium and zinc) than to produce deformation by means of the slip planes. The physical properties of metals are greatly influenced by these internal changes ; their conductivity, electromotive properties, the rate of solution and, above all, their elastic limit, all undergo a change. Cold-working increases the elasticity of copper fourteen times. There is, moreover, a difference between the lower and upper elastic limits—the former is the limit at which the metal first undergoes a lasting deformation, while at the latter the metal begins to rupture. This is not necessarily a breaking up into pieces, but can also take the form of the flowing of the crystal. The coherence of the particles of metal which are above the upper elastic limit is greatly lessened, but between the upper and lower limits the particles are forced closer together, a fact which may be of great importance. The hardness of the individual elements composing the metal is not substantially affected, but their power of cohesion is increased.

Recrystallisation.—If in the mechanical treatment of a metal the process is arrested the metal will tend to regain its former properties when left to itself, and the lamellæ formed tend to disappear ; the crystallites return, more or less, to their original state. This process, which is called "recrystallisation," is caused, according to Tammann, by the surface tension of the lamellæ. These undergo a shrinkage, facilitated by their thinness.[1] The thickening of the particles thus occasioned must not be confused with the effects due either to the formation and growth of new nuclei or the amalgamation of small crystals. The recovery of the crystallites and the nuclei sometimes takes place at the same temperature, as in silver ; but sometimes the temperatures are very different, as in tungsten, in which the original properties are lost at $1100°$, while the new nuclei appear at $1500°$.

The surface tension decreases with rising temperature, and thus at high temperatures the thick lamellæ will also be forced to shrink. At every temperature there is a limit to which the lamellæ can shrink, and only those lamellæ will be welded together whose tensile strength is less than their surface tension. The temperature of recrystallisation depends on the thickness of the lamellæ, and the greater the number of lamellæ into which the metal is split up the more readily will it recrystallise ; this partly accounts for the variations in the elasticity of metals with changes of temperature (tempering).

Besides the methods of cold-working and the quenching from high temperatures, as in the hardening of steel, which results in the preservation of the γ-form of iron below the transition point, other methods of conferring desirable properties on metals are used. For instance, the metal is alloyed with small quantities of other metals at a high temperature, quenched and left cold for some time. Wilm[2] found that the hardness and tensile strength of aluminium were improved if the alloy with 3 per cent. Cu, 0·5 per cent. Mg, and 0·5 per cent. Mn was quenched from $500°$ and then left for eight days at the ordinary temperature. In this and in similar cases (Fe—C, Cu—Be) the alteration in properties depends on the disintegration at low temperatures of the supersaturated solutions formed when hot. The temperature and time optima for the changes in elasticity, conductivity, and magnetic properties are not the same, as the stretching of the space lattices of the ground metal affects these properties differently (see Masing, *Z. Elektrochem.*, 1931, **37**, 414).

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[1] The correctness of this explanation is not universally accepted.

[2] *Metallurgie*, 1911, **8**, 225.

CHAPTER VI

PREPARATION OF ELEMENTS—NON-METALS

*Hydrogen—The electrometric series—Deuterium—Halogens—Oxidation and reduction
—Oxygen—Sulphur, selenium, tellurium—Nitrogen—Phosphorus—Boron, silicon,
titanium—The inert gases*

SOME elements only occur free in nature in small quantities or in such
complex mixtures with other substances that they cannot readily be
purified; it is then necessary to prepare the elements from compounds.
There are two general methods of preparing elements from their
compounds:

1. *Decomposition.*—The compounds may decompose spontaneously
   or on heating or with other treatment, and the elements are
   formed as products of the decomposition.
2. *Displacement.*—Some other substance replaces the element in
   the compound and thus sets it free.

The special methods of preparing elements all come under one of these
two headings.

Preparation of Hydrogen[1]

1. DISPLACEMENT METHODS

These methods are of great importance in the preparation of
hydrogen. The hydrogen may be derived either from (*a*) hydrogen
ions or from (*b*) hydrogen compounds which are not ionised.

(*a*) *Preparation from Hydrogen Ions.*—The electromotive series of
the elements indicates quantitatively their affinity for electric charges.

The table on p. 151 gives the E.M.F. in volts produced by electrodes of the
various elements against a normal hydrogen electrode at room temperature. The
electrolyte surrounding the electrode which was being tested contained the ion of the
substance of the electrode in a concentration of one g. ion per litre. The potentials
of the elements printed in *italic* are derived from the melts of the halides[2] and
extrapolated to 18°.

The elements are usually arranged so that the affinity for negative
charges increases progressively in passing from the top to the bottom

[1] In this section the name hydrogen will be retained for the unseparated mixtures
of H and D, chiefly H, which are prepared from natural sources of these isotopes;
if only $^1_1$H is meant it will be referred to as *protium.*

[2] Neumann and Richter, *Z. Elektrochem.*, 1925, 31, 287.

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of the series; the tendency to form positive ions in solution therefore decreases in going down the series. Thus hydrogen ions give up their positive charges to any element which stands above hydrogen in the electrical series; the more widely separated the second element is from hydrogen the greater is the tendency to discharge $H^{\cdot}$ ions, the property reaching a maximum with caesium.

Electrometric Series of the Elements

Cs	− 2.91	Be	− 0.81	As	+ 0.3
Rb	− 2.74	Zn	− 0.76	Cu``	+ 0.34
K	− 2.61	Ga<	− 0.76	Re*	+ 0.60
Na	− 2.45	Cr``	− 0.6	Ag	+ 0.80
Ba	− 2.15	Fe``	− 0.43	Hg``	+ 0.80
Ce```	− 2.10	In >	− 0.40	Pd	+ 0.82
Li	− 2.09	Cd	− 0.40	Pt >	+ 0.86
Sr	− 2.07	Tl`	− 0.33	Au`	+ 1.5
Ca	− 1.90	Co``	− 0.29		
La	− 1.75	Ni	− 0.22	Te	− 0.84
Th	− 1.75	Pb	− 0.12	S	− 0.55
Nd	− 1.65	Sn``	− 0.10	O	+ 0.39
Mg	− 1.55	H	− 0.00	I	+ 0.54
Pr	− 1.44	Sb	+ 0.1	Br	+ 1.08
Al	− 1.28	Bi	+ 0.2	Cl	+ 1.36
Mn	− 1.0	Ce````	+ 0.24	F	+ 1.92

* Electrolyte: $2N\mathrm{H_2SO_4}$.

The normal potentials of the elements show a pronounced periodicity dependent on their position in the periodic system—the curve reaching its highest points with the alkali metals, its lowest with the halogens, with a single span in each of the first three periods, and with two in each of the long periods. It is, naturally, discontinuous at the inert gases.

The preparation of hydrogen from the ionic state by the displacement method therefore involves bringing these ions into contact with an element preceding hydrogen in the electrical series. The method sometimes fails, owing to the influence of physical conditions; e.g. the more electropositive element may form an insoluble product which adheres to its surface, thus protecting the bulk of the metal from further action of the hydrogen ions. Under such conditions the evolution of hydrogen starts briskly, but soon falls off, and finally ceases when the surface of the metal becomes completely covered with the protective layer.

Pure water contains a small quantity of hydrogen ions, together with an equivalent quantity of hydroxyl ions. If the hydrogen ions are discharged by interaction of water with more electropositive metals, the resulting metallic ions tend to associate with the hydroxyl ions to form metallic hydroxides. Soluble hydroxides have no detrimental effect upon the progress of the reaction; but an insoluble

or slightly soluble hydroxide forms a coating on the surface of the metal which prevents any further action.

This reaction can be made to proceed further by decreasing the number of hydroxyl ions in the water. Thus the addition of acid introduces an excess of hydrogen ions into the solution, which produces a reduction in the quantity of hydroxyl ions in accordance with the law of mass action. The quantity of these ions may become so small that the solubility product of the metallic hydroxide is not reached, and the hydroxide is therefore not precipitated; secondary changes, such as salt formation, may also be operative.

The alkali metals are therefore readily attacked by water, even in the cold, and hydrogen can be prepared by the action of water on these metals, and, to a lesser extent, on the alkaline earth metals. Metals which occupy a lower position in the electrical series are at the most only slightly attacked by water. Magnesium hydroxide has a very low solubility product; on treatment with water the metal soon becomes covered with a film of precipitated hydroxide and the evolution of hydrogen ceases; but the reaction proceeds fairly vigorously when boiling water is used, since the magnesium hydroxide is then more soluble, or if a solution of magnesium chloride is used instead of water. Hydrogen is preferably obtained by the action of dilute acids, usually HCl or H_2SO_4, on metals such as Mg, Al, Zn, Fe, etc.

Addition of acids is not the sole method of reducing the quantity of hydroxyl ions in a solution; e.g. the addition of ammonium chloride serves the same purpose. A steady stream of hydrogen is evolved by the interaction of zinc and a solution of this salt. The hydroxyl ions and ammonium ions mutually discharge one another with production of undissociated ammonium hydroxide, the greater portion of which decomposes into ammonia and water: $NH_4{}^{\cdot} + OH' \longrightarrow NH_4OH \longrightarrow NH_3 + H_2O$. The concentration of hydroxyl ions becomes so minute that zinc hydroxide is no longer precipitated. Ammonium salts thus resemble acids in dissolving most metals which are electropositive to hydrogen. Aluminium is an exception, owing to the extreme insolubility of aluminium hydroxide, in consequence of which the hydroxyl ions still left in solution are sufficient to cause its precipitation.

The method, with a suitable modification, can even be applied to aluminium; the latter is used in the form of an alloy with a less electropositive metal, e.g. mercury. This combination acts as a galvanic couple; hydrogen ions are discharged by the aluminium and the hydrogen gas evolved from the surface of the mercury. The precipitated hydroxide obviously adheres less tenaciously to the surface of the couple than to pure aluminium, and as the layer is discontinuous further action takes place. The fresh surface of aluminium immediately alloys with the mercury. Large quantities of aluminium can thus be dissolved by admixture with a very small proportion of mercury.

A similar reaction occurs with the water vapour of the air; if amalgamated aluminium sheets are exposed to damp air they gradually become crusted with polyp-shaped growths of aluminium hydroxide to a thickness of about one centimetre. The crust is continually pushed upwards, owing to the formation of more hydroxide underneath on the surface of the metal, and consequently assumes the characteristic appearance of "sprouted alumina." The use of aluminium amalgam is of special importance, as the gas is liberated from perfectly neutral solutions, and no acidic or alkaline products are formed.

Various other combinations of metals have been much used for preparing hydrogen. The zinc-copper couple reacts in the same way as aluminium amalgam, and is an important reducing agent. The couple consists of zinc, on the surface of which copper has been deposited. Hydrogen is evolved very slowly by the action of water on this couple, thus ensuring thorough contact with the compound to be reduced. The slowness of the reaction favours the production of nascent hydrogen.

The ease with which metals can displace hydrogen from solution does not always correspond to their positions in the electrical series of the elements; such anomalies may often be traced to the disturbing influence of concentration on the order of the metals in the series. The list of elements already given relates only to normal solutions, and is not valid for other concentrations. The electro-affinity of metals is also very greatly affected by the presence of impurities which tend to set up small galvanic couples. The position of a metal in the electrical series cannot be determined even approximately when it forms a chemical compound with the impurity.

When very pure metals are used in the preparation of hydrogen, the gas is evolved extremely slowly, owing to the absence of galvanic couples; e.g. zinc which has been carefully purified has almost no action on sulphuric acid. If, however, the zinc is touched with a platinum wire, the voltaic combination, zinc—solution—platinum, is produced and there is a sudden increase in the evolution of gas. The zinc, in consequence of its high solution pressure, tends to dissolve, and sends positive ions into solution, which exert a repulsive force on the positively charged hydrogen ions; the discharge of these ions at the zinc electrode—which is of course negatively charged owing to the loss of positive ions—takes place extremely slowly. With the zinc-platinum couple, this negative electricity escapes to the platinum and there neutralises the charges on the hydrogen ions.

Little or no hydrogen is liberated by the action of concentrated acids on metals. Iron does not dissolve to an appreciable extent in concentrated sulphuric acid owing to the formation of a black deposit on the surface of the iron, which protects the metal from further action. Other metals dissolve slowly in strong acids. This comparative passivity sometimes originates in part from the presence of a gaseous or solid film

on the surface of the metal, which prevents free access of the acid; the phenomenon is also due to the small number of ions present in concentrated acids. Since ionic reactions are generally almost instantaneous, the ions originally present are soon used up; the electrolytic equilibrium is maintained by the ionisation of further quantities of undissociated acid, but the high viscosity of concentrated acids also helps to retard these reactions. The evolution of hydrogen is proportional to the quantity of hydrogen ions which come in contact with the metal surface; provided the metal supplies the necessary ions, the formation of gas on the electrode surface is practically instantaneous. The ions, under experimental conditions, have to diffuse through the electrolyte in order to reach the electrode, and the time required for this migration is proportional to the viscosity of the medium. Powdered metals dissolve more quickly than coarse lumps, since in the former condition they present a much larger surface to the action of the ions in solution. The increase in the speed of the reaction produced by rise of temperature is chiefly due to the lower viscosity of hot liquids rather than to increased dissociation of the acids. In the passive state the tendency of the metal to form positive ions is largely suppressed, and the fact that metals do not readily give hydrogen with concentrated acids is to some extent dependent on this property. For example, when iron is dipped into concentrated nitric acid, it becomes passive and is then unable to discharge copper ions, and if placed in a solution of copper sulphate does not become coated with a layer of copper. The passivity can, however, be removed by hammering the iron or by electrolytic reduction.

The rate at which certain metals dissolve in acids is subject to abrupt fluctuations. At times the reaction becomes very vigorous and is accompanied by a sudden increase in the evolution of gas; during the alternate periods the evolution of hydrogen almost ceases. The action of nitric acid on iron which has been previously treated with a silver solution, and of acids on chromium prepared by the Goldschmidt process, are examples of such behaviour.[1] Hedges and Myers[2] have found that this phenomenon is general when metals dissolve with evolution of hydrogen, and that it occurs only in presence of a third substance which acts as catalyst. The third substance may be either a foreign metal or a colloid, and the necessary quantity is so small that it can be provided from the substance of the reaction vessel. The frequency of the period depends on the quantity of catalyst and increases with rise of temperature; it is greatly reduced by small quantities of the usual catalyst poisons. This phenomenon can be observed when Zn, Fe, Al, Mg, Mn and Cd dissolve in hydrochloric acid, when Zn and Al dissolve in other acids, in alkalis and in salt

[1] Ostwald, Z. physikal. Chem., 1900, 35, 33, 204.

[2] J. Chem. Soc., 1924, 125, 604.

solutions, when sodium amalgam acts on water or metallic sodium on various alcohols, in the evolution of hydrogen from solutions of $CrCl_2$ in presence of platinum, and in many other reactions.

Weak acids, including most organic acids, carbonic acid, etc., have no perceptible action on metals. The opposing force is of exactly the same nature as that which impedes the interaction of metals with water, and is not caused by the deficiency of hydrogen ions. A protective layer of basic salt is formed on the surface of the metal. A film of almost insoluble basic carbonate on the metal surface quickly arrests the action of carbonic acid, *e.g.* on lead. The weaker the acid the more readily is the protective film formed, since the salts of very weak acids are almost completely hydrolysed in solution.

Like all ionic reactions, that between a metal and hydrogen ions is reversible : $M + H^{\cdot} \rightleftharpoons M^{\cdot} + H$. Unless the quantity of hydrogen thus set free is more than sufficient to saturate the solution, no gas will be evolved, the equilibrium is not disturbed, and no further production of hydrogen takes place. Such conditions are exceptional, owing to the slight solubility of hydrogen in liquids ; this solubility can be diminished by working under reduced pressure, and thereby increasing the rate of gas evolution. High pressures displace the equilibrium in favour of the reverse reaction : $H + M^{\cdot} \longrightarrow H^{\cdot} + M$, and noble metals are precipitated by passing a stream of hydrogen under pressure through solutions of their salts.[1]

Hydrogen ions can also be discharged electrolytically without the intervention of chemical reagents ; the opposite charges neutralise one another :

$$H \oplus + \ominus \longrightarrow H + \oplus \ominus, \text{ or } H^{\cdot} + \textcircled{e} = H$$
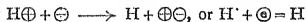
As a result of its low solubility, small currents of electricity are able to start the evolution of hydrogen, but in certain circumstances the evolution of gas is retarded by polarisation and over-voltage. These phenomena are discussed in text-books of electro-chemistry. The smoothness or roughness of the electrode surface, as well as the chemical nature of the electrode material, has an important influence on the rate of evolution of the gas.

The charge on hydrogen ions can also be removed by positive ions, of which the tendency to take up positive or lose negative charges is stronger than the attraction of $H^{\cdot}$ ions for their own charges. There are, however, few examples of this type of reaction. Hydrogen is liberated from aqueous solutions of bivalent chromium and vanadium salts, which are thereby converted to the tervalent condition. Compounds of bivalent samarium and of tungsten behave similarly. $K_4Co(CN)_6$ liberates hydrogen when dissolved in water and is transformed into $K_3Co(CN)_6$. The cations of these compounds thus

[1] Ipatiev, *Ber.*, 1909-1912, 42-45.

precede hydrogen in the electrical series of the elements. The peculiarity of these reactions is the slow evolution of hydrogen, while methods which involve a simple exchange of charges proceed much more quickly. The difference of speed is caused by intermediate reactions which occur during the former processes. It is possible that chromous compounds, like mercurous derivatives, tend to break down into the metal and the salts of a higher oxide; the metal then reacts with the water. The principle underlying this method of preparation is thus identical with that involved in the production of hydrogen from its ions by the direct action of metals.

The displacement of hydrogen from ammonia, $H.NH_2$, resembles that from water, $H.OH$. The alkali and alkaline earth metals attack ammonia, forming an amide and liberating hydrogen: $2K + 2NH_3 \longrightarrow 2KNH_2 + H_2$. This reaction, however, does not take place at low temperatures, when the metal goes into solution without evolution of hydrogen, and in some instances the liquid contains a complex ammine, $M(NH_3)_x$. At a higher temperature these derivatives decompose into amide and hydrogen (cf. p. 625).

(b) *The Displacement of Hydrogen from other Compounds.*— Hydrogen is liberated from alkali hydroxides by the action of metals. For example, fused caustic soda evolves hydrogen on treatment with the alkali metals: $2NaOH + 2Na \longrightarrow 2Na_2O + H_2$. Similarly, zinc dust can displace the element from calcium hydroxide at a red heat: $Ca(OH)_2 + Zn \longrightarrow CaO_2Zn + H_2$.

The displacement of hydrogen is also effected by the interaction of the aqueous solutions of the alkaline hydroxides and metals which can form anions containing oxygen, e.g. Zn and Al:

$$2NaOH + Zn \longrightarrow Zn(ONa)_2 + 2H; \quad 3NaOH + Al \longrightarrow Al(ONa)_3 + 3H.$$
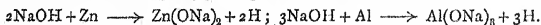
These reactions take place energetically in the cold. It is possible that even in these methods the hydrogen results from the discharge of its ions, for aqueous and even fused caustic soda contains minute quantities of $H^{\cdot}$ ions; i.e. the base functions as an "acid." The sodium, however, is the basic component of the metallic products "sodium zincate" and "sodium aluminate," which dissociate into the ions $Na^{\cdot}$ and ZnO_2'', $Na^{\cdot}$ and AlO_3''' respectively.

The hydrogen of alkali hydroxides can also be replaced by certain non-metallic elements, particularly those which form allotropes of a metallic appearance: e.g. silicon and boron react with caustic soda; the reactions may be represented according to the equations, which, however, are not strictly accurate:

$$Si + 4NaOH \longrightarrow Si(ONa)_4 + 4H; \quad B + 3NaOH \longrightarrow B(ONa)_3 + 3H.$$
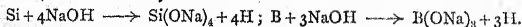
The alkali may be used in the fused state or in aqueous solution, and ferrosilicon can be used in place of the pure element.

The non-metals belonging to Groups VI and VII of the periodic system have a strong chemical affinity for hydrogen and are therefore of no use for the preparation of this element. The affinity of the non-metals of Group V for hydrogen is of intermediate strength; *e.g.* free hydrogen is obtained as well as phosphine by the action of phosphorus on caustic soda; the phosphorus thus shows analogies with both silicon and chlorine in its behaviour towards alkalis.

Metallic hydrides can also be employed for the preparation of hydrogen by the displacement methods. These compounds, on hydrolysis, give the metallic hydroxide and hydrogen: $NaH + H_2O \longrightarrow NaOH + H_2$; $CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + 2H_2$. The reaction is thus one of double decomposition like that between chlorine and methane; the only difference is that in the former reaction the same product—hydrogen—is liberated from both the substances.

Hydrogen is produced by the action of aqueous alkalis on the silicon and boron hydrides (see p. 769), and also by fermentation processes (*e.g.* of starch by the Fernbach bacillus).

2. DECOMPOSITION METHODS

These methods of preparation are of less practical importance than the foregoing, as suitable compounds are not readily obtained and, even when available, often decompose at inconvenient temperatures. Compounds which may be used include H_2O, H_2S, NH_3, HBr, HI, AsH_3, NaH, CaH_2 and some hydrocarbons. Many of the endothermic hydrides break down spontaneously, *e.g.* hydrogen iodide and arsine; with acetylene, however, sparking or heating is necessary. High temperatures are required for the decomposition of the exothermic compounds. All these reactions result in the formation of equilibrium mixtures, in accordance with the laws governing reversible reactions, unless one of the products of decomposition is removed from the reaction zone.

The two reactions:

$$\text{I. } 2HI \rightleftharpoons H_2 + I_2, \qquad \text{II. } 2NH_3 \rightleftharpoons N_2 + 3H_2,$$
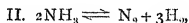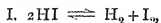
are both influenced by changes of temperature. Reaction (I) does not involve a change in the number of gaseous molecules, and the position of equilibrium is therefore independent of the pressure. Reaction (II) is affected by changes of pressure, since the decomposition of ammonia is attended by an increase in the number of molecules. These chemical actions, being reversible, obey the law of mass action. The degree of dissociation is therefore increased by the removal of one of the products (in practice, iodine) from the gaseous mixture.

The continual removal of one of the dissociation products results in the complete decomposition of the original compound. The elimination may be carried out chemically, but sometimes, owing to polymerisation,

the constituent concerned undergoes a change of state, with formation of a non-volatile solid. Thus the spontaneous decomposition of arsine involves the two processes :

$$\text{I. } AsH_3 \rightleftharpoons As + 3H. \qquad \text{II. } 4As \longrightarrow As_4.$$

Silane behaves similarly when heated :

$$\text{I. } SiH_4 \rightleftharpoons Si + 4H. \qquad \text{II. } xSi \longrightarrow Si_x.$$
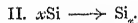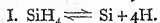
Such secondary changes are of frequent occurrence; a quantitative yield of hydrogen is obtained, provided the secondary reaction goes to completion. If, however, the side reaction is itself reversible, equilibrium will be established in the main reaction. For example, the dissociation of hydrogen iodide is followed by the production of diatomic molecules of iodine :

$$\text{I. } HI \rightleftharpoons H + I. \qquad \text{II. } 2I \rightleftharpoons I_2.$$
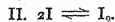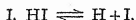
The iodine vapour still contains a sufficient proportion of iodine atoms for the regeneration of hydrogen iodide. The halogen solidifies on lowering the temperature, and then the quantity of free iodine atoms in the gaseous mixture is so minute that the decomposition of the hydrogen iodide proceeds almost to completion.

There are other secondary changes besides polymerisation which may hinder the regeneration of the hydrogen compound. Many organic bodies on heating evolve hydrogen, but these reactions are usually irreversible, since the remainder of the molecule undergoes a profound change and the new compound which results is unaffected by hydrogen. Also, the hydrogen when first liberated is in the atomic condition but quickly changes, irreversibly under the conditions of experiment, into molecular hydrogen, which of course does not possess the same chemical activity as the nascent substance. The equilibria set up are confined to the primary products of decomposition, and are disturbed by any subsequent transformation which these may undergo.

Complete decomposition of hydrogen compounds can also be effected by chemical methods. If, for instance, carbon is brought in contact with the equilibrium system : $2H_2O \rightleftharpoons 2H_2 + O_2$, the oxygen is continually used up, forming carbon monoxide or dioxide; the equilibrium is maintained by the further dissociation of the water, and eventually the whole of the hydrogen is liberated. The manufacture of water gas (p. 785) is based on this principle, although various modifications can be made in the foregoing reaction. Coal may be heated to redness with some substance which yields water, such as calcium hydroxide or carbon monoxide passed over heated calcium hydroxide; in the reaction which occurs the monoxide unites with the oxygen. A third method consists in passing steam over calcium carbide; the oxygen is then absorbed by the calcium as well as by the carbon.

Preparation of Deuterium

Urey, Brickwedde and Murphy,[1] who were the first to detect deuterium by an examination of the Balmer series of the hydrogen spectrum, obtained a partial separation of H and D by the fractional distillation of liquid hydrogen. The different rates of diffusion of H_2 and D_2 can also be utilised; for example, spectroscopically pure D_2 was obtained by diffusion from a mixture of H_2 and D_2 resulting from the electrical decomposition[2] of HD.

A. and L. Farkas[3] allowed H : D (3 : 2) to diffuse through palladium at 270°; the residue contained H : D = 2 : 3. Some separation was also obtained when H_2 and D_2 were allowed to effuse under low pressure. Partial separations have also been effected by the adsorption of water or of hydrogen on charcoal, and fractional distillation and freezing of water also leads to slight concentration of deuterium. After lying in bright sunshine, snow shows a slight increase in density.

Chemical methods can also be used. Thus if zinc is dissolved in sulphuric acid (0.1 per cent.), with a 25 per cent. deuterium content, the gas evolved[4] contains only 8 per cent. of D_2. These authors found the extent of separation was less if Na, Ca and Al are used, but Hughes, Ingold and Wilson[5] showed that the separation, both for these and other metals, depends upon such factors as the pH of the solution; the best separation, although only partial, was obtained by dissolving a 50 per cent. zinc-copper couple in dilute sulphuric acid. When $[Co(NH_3)_6](NO_3)_3$ is dissolved in heavy water there is a slow replacement of the H of the NH_3 groups by deuterium.[6]

The most effective and complete separation is achieved by the electrolysis of alkaline aqueous solutions (see p. 396). Pure D_2 can be obtained from the pure D_2O, so prepared, by any of the reactions commonly used for the preparation of hydrogen from H_2O.

Attempts have been made to isolate the hydrogen isotope ^3_1H (*tritium*) by the electrolysis of alkaline heavy water. The vapour of water so treated fails to show the presence of tritium in the mass spectrograph (Aston). This result conflicts with that obtained by Bleakney and it must be supposed that the quantity of tritium in ordinary hydrogen is negligibly small.[7] The production of this isotope by the bombardment of deuterium with deuterons is quite marked, the atom ^3_2He being formed by a secondary disintegration (see p. 87).

[1] *Physical Rev.*, 1932, [ii.], 40, 1.   [2] Hertz, *Naturwiss.*, 1933, 21, 884.
[3] *Nature*, 1933, 132, 894.   [4] A. and L. Farkas, *Nature*, 1934, 133, 139.
[5] *Nature*, 1934, 133, 291 ; *J. Chem. Soc.*, 1934, 493.
[6] Briscoe, Anderson and James, *Nature*, 1937, 139, 109.
[7] Rutherford, *Nature*, 1937, 140 303.

Preparation of the Halogens

1. Decomposition Methods

The ease with which the halogens are liberated by direct decomposition of their compounds increases in the order of atomic weights. The heat of formation of the iodides is nearly always less than that of the other halides, and consequently less external energy suffices for their decomposition. The following table gives the heats of formation of a few halogen compounds, illustrating the progressive diminution in passing from fluorine to iodine:

Heat of Formation of Halogen Compounds

HF (gas)	HCl (gas)	HBr (gas)	HI (gas)*
35·8	22·0	8·5	− 6·2 Cal.
	PCl_3 (liq.)	PBr_3 (liq.)	PI_3 (solid)
	76	45	11 Cal.
SiF_4 (gas)	$SiCl_4$ (liq.)	$SiBr_4$ (liq.)	SiI_4 (solid)
240	128	71	6·7 Cal.
SbF_3 (solid)	$SbCl_3$ (solid)	$SbBr_3$ (solid)	SbI_3 (solid)
141	91	61	29 Cal.
PbF_2	$PbCl_2$	$PbBr_2$	PbI_2
108	83	64	40 Cal.
KF	KCl	KBr	KI
118	106	95	80 Cal.

* Using solid iodine; with gaseous iodine the reaction is slightly exothermal.

Since the liberation of the halogen from these compounds is a reversible process, the position of equilibrium indicates the relative stability of the derivative. The percentage decomposition of the halogen hydracids at 600° T. is:

HCl	HBr	HI
0·0000015	0·0035	18·9 per cent.

The stability of a series of halides formed by the same element decreases as the proportion of halogen increases. Thus when a chloride in which the metal possesses more than its minimum valency, is treated with potassium iodide, a lower iodide and free iodine are formed. For example, FeI_3 is not produced by the action of KI on $FeCl_3$, as it at once breaks down into Fe_2I_3 and free iodine. Similarly, cuprous iodide and iodine are formed by the interaction of potassium iodide and cupric chloride: $Cu^{II}Cl_2 + 2KI \longrightarrow Cu^I I + I + 2KCl$. (This reaction is reversible, but the position of equilibrium is well on the side of formation of free iodine.)

The stability of the halides increases with rise in the atomic volume as well as in the atomic weight of the element combined with the halogen. Many elements exhibit a higher valency towards fluorine than towards chlorine, and the maximum valency towards the latter element often exceeds that reached with the bromides (cf. p. 59). Halides of both

metals and non-metals become increasingly unstable in passing from the fluorine derivatives to those of iodine.

Fluorine is therefore prepared with the greatest difficulty by the decomposition method. MnF_3 when heated decomposes into fluorine and MnF_2; the element also appears to be isolated by the action of heat upon double fluorides[1] containing PbF_4, but both these processes are unsatisfactory. Iodine, on the other hand, is readily obtained by decomposition methods, often without the aid of heat. Thus the endothermic compound hydrogen iodide decomposes slowly in the dark at ordinary temperatures; the velocity of decomposition is much greater under the influence of light. This change is irreversible at normal temperatures, owing to the low vapour pressure of solid iodine, and hence the liberation of iodine is quantitative.[2]

The quadrivalent derivatives of manganese with chlorine and bromine are formed as intermediate products in the preparation of these elements by the action of hydrochloric or hydrobromic acids on pyrolusite. A dark brown liquid which contains $MnCl_4$ and H_2MnCl_6 is formed by the interaction of concentrated hydrochloric acid and manganese dioxide in the cold: $MnO_2 + 4HCl \longrightarrow MnCl_4 + 2H_2O$. The liquid decomposes slowly on standing and more rapidly when heated, with evolution of chlorine: $MnCl_4 \longrightarrow MnCl_2 + Cl_2$. The formation of bromine by the treatment of pyrolusite with hydrobromic acid is exactly similar in principle, but the reaction proceeds more easily than with hydrochloric acid. The action of hydriodic acid on pyrolusite with liberation of iodine is more vigorous than that of either of the other halogen acids. These methods may be modified by using a mixture of sulphuric acid and a halide instead of the free halogen hydracids. Other higher oxides can be used instead of pyrolusite, e.g. lead dioxide, PbO_2. The principle of the reactions is not altered, and the first product formed by the treatment of lead dioxide with HCl is $PbCl_4$ which quickly decomposes into $PbCl_2$ and Cl_2. Lead dioxide, like pyrolusite, is attacked more readily by the heavier halogen hydracids.

The quantity of $MnCl_4$ or $PbCl_4$ formed by the decomposition of pyrolusite or lead dioxide with hydrochloric acid is very small. The principal intermediate product is an addition compound of the tetrahalide with hydrochloric acid:

$$MnCl_4 + 2HCl \longrightarrow H_2MnCl_6 \qquad PbCl_4 + 2HCl \longrightarrow H_2PbCl_6.$$

These derivatives, however, subsequently lose a small part of the hydrochloric acid. It is probable that the liberation of chlorine is proportional to the quantity of free tetrachloride present, since the addition products are more stable than the simple halides. The salts of these "halogeno-acids" are also much more stable than the tetrachlorides. Thus free $MnCl_4$ has not been isolated, but K_2MnCl_6 can be preserved for a considerable time. Similarly $PbCl_4$ decomposes slowly at ordinary temperatures, while K_2PbCl_6 can be heated above 100° without decomposition. The aurichlorides,

[1] Ruff, Z. anorg. Chem., 1916, 98, 27.
[2] Bodenstein, Z. physikal. Chem., 1897, 22, 23.

e.g. $KAuCl_4$, are also more stable than the parent compound, $AuCl_3$. When heated, gold trichloride readily breaks up into $AuCl$ and Cl_2, exerting a vapour pressure equal to one atmosphere at 290°, while even at 440° $KAuCl_4$ has a pressure equal to only one-half of an atmosphere.

These complex halogen acids and their salts resemble the simple halides in being more stable when the atomic weight of the halogen is less. Thus the double fluorides are by far the most stable of these salts. Silicofluoric acid and the silicofluorides are well-defined compounds, but the chlorine derivative H_2SiCl_6 is unknown. Stable salts of titanifluoric acid, H_2TiF_6, have also been obtained, but the other complex halides of titanium are extremely unstable. Similarly, the element boron forms a characteristic acid, HBF_4, and the corresponding salts termed borofluorides, but both the acid $HBCl_4$ and its salts are unknown. The complex halogen derivatives of the metals show a similar gradation in stability ; thus the salts of the acid $HSbCl_6$ are stable, those of $HSbBr_6$ readily lose bromine, while scarcely any iodo-salts have been isolated. K_2PtCl_6 can be heated to a temperature of 400° without decomposition, while K_2PtI_6 decomposes at 100°. Many other examples could be given which illustrate the decrease in stability of these compounds in passing from fluorine to iodine. The formation of the free halogens from the halogeno-acids by the decomposition method therefore takes place more easily as the atomic weight (or atomic volume) of the halogen increases.

2. DISPLACEMENT METHODS

Oxidation and Reduction.—The formation of a non-metal in the free state by substitution methods invariably requires the application of an oxidising agent. The term oxidation formerly denoted the addition of oxygen to a compound, or the abstraction of hydrogen from it. The modern definition of oxidation, however, regards such reactions as particular examples of a large class of chemical changes. The process of oxidation denotes :

1. Increase in valency of an element in its compounds with electronegative elements. When $FeCl_2$, for example, is converted into $FeCl_3$, the iron is said to be oxidised from the bivalent to the tervalent condition. The union of As_2S_3 with sulphur, forming As_2S_5, the production of calcium nitride, Ca_3N_2, from metallic calcium and nitrogen are examples of a similar type of oxidation ; in the latter reaction, calcium, which must be regarded as non-valent in the metallic condition becomes bivalent in the nitrogen compound. The element which acquires the increased valency may itself be a non-metal ; thus, sulphur when converted into SO_2 undergoes oxidation, becoming quadrivalent ; the production of SO_3 from SO_2 carries the oxidation a stage further.

2. A decrease in the valency of an element in its compounds with electropositive elements. Thus the liberation of sulphur by the removal of hydrogen from sulphuretted hydrogen involves the oxidation of sulphur. Similarly, chlorine is oxidised by the decomposition of gold chloride into its elements.

Oxidation takes place at the anode during electrolytic reactions ; the metals of which this electrode are made dissolve in the electrolyte with formation of ions, and consequently their valencies are increased,

During oxidation processes the element which is oxidised is deprived of electrons. This change in electrical condition occurs at the anode during electrolysis, and is effected chemically by reaction with a compound which has a stronger affinity for electrons than the one to be oxidised.

In the examples given there is either an increase in the positive charge of the element undergoing oxidation:

$$\overset{\text{II}}{\text{Fe}}\text{Cl}_2 \longrightarrow \overset{\text{III}}{\text{Fe}}\text{Cl}_3 \quad \overset{\text{III}}{\text{As}_2}\text{S}_3 \longrightarrow \overset{\text{V}}{\text{As}_2}\text{S}_5 \quad \overset{\text{II}}{\text{Ca}} \longrightarrow \text{Ca}_3\text{N}_2 \quad \overset{\text{IV}}{\text{SO}_2} \longrightarrow \overset{\text{VI}}{\text{SO}_3},$$
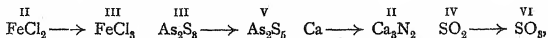
or the negative charge is diminished:

$$\overset{''}{\text{S}}\text{H}_2 \longrightarrow \text{S} \qquad \overset{'}{\text{Cl}}\text{Au} \longrightarrow \text{Cl}.$$

Oxidation is therefore defined as a process which involves an increase in the number of positive charges, or a diminution in the number of negative charges on an atom.

Reduction is the converse of oxidation, involving a diminution in the number of positive charges, or an increase in the number of negative charges on an atom. The reverse reactions to those which have been selected as oxidation processes are examples of reduction; thus the transformation of ferric iron to ferrous iron, the combination of sulphur with hydrogen, etc., are processes of reduction. Hydrogen has a tendency to form positive ions, and therefore behaves as a reducing agent.

It is obvious that oxidation and reduction must always occur simultaneously. The element or compound which has been reduced gains electrons from some other element or compound, which is thereby oxidised. It is not strictly accurate to describe the change represented by the equation $2\text{FeCl}_2 + \text{Cl}_2 \longrightarrow 2\text{FeCl}_3$ merely as an oxidation reaction. The ferrous ion is of course oxidised, but it is equally true to say that the chlorine is reduced. Many reactions which involve oxidation-reduction are regarded as oxidation processes, if the accompanying reduction is of subordinate interest. In the present example it is the oxidation of ferrous iron to the ferric condition which is usually of practical importance.

The electrical series of the elements, in which they are arranged in order of affinity for positive electricity, has been discussed on p. 151. It will now be evident that the series also indicates the relative strengths of the oxidising and reducing powers of the elements. The higher the position of an element in the electrical series the greater the tendency to lose electrons, and therefore the more powerful the reducing action upon ions. A metal displaces those which follow it in the electro-chemical series from solutions of their salts, provided no secondary reactions take place with the water; e.g. zinc precipitates copper in the metallic form from solutions of its salts; the positive charges of the cupric ions are transferred to the zinc. The ionised radicals of compounds can also be arranged according to their oxidising and reducing capacity.

Every reaction involving an exchange of electrical charges is an oxidation-reduction reaction, and is thus compounded of two simple processes, each of which has its characteristic electric potential. The method of measurement of the electromotive force of such processes is, at first sight, not obvious. If, however, the oxidation carried out is always of the same reducing agent, *e.g.* a platinum electrode saturated with hydrogen and immersed in a solution of normal $H^{\cdot}$ ion concentration, the reduction potential is constant; hence the relative values of the E.M.F. are determined by the potential difference at the oxidising pole. The E.M.F. of cells of the type

<p style="text-align:center">$H^{\cdot}$ electrode/electrolyte/oxidising agent</p>

is directly proportional to the power of the oxidising agent. (For details see text-books of physical or electro-chemistry.)

The hydrogen electrode functions as the negative pole in contact with some electrolytes, and then the hydrogen ions tend to give up their positive charges, with production of free hydrogen gas: the ions are therefore themselves reduced. Hydrogen occupies an intermediate position in the electrical series of the elements; consequently it acts as an oxidising agent towards the metals which precede it, and as a reducing agent towards those which follow it in the series. The arrangement of oxidising and reducing agents in the order of their single potential differences referred to the normal hydrogen electrode shows on which reagents any one member of the series will exert an oxidising influence, and on which it will exert a reducing effect. The terms "oxidising agent" and "reducing agent" are relative; whether a compound behaves as an oxidising or reducing agent depends upon the nature of the substance with which it is brought into contact.

The oxidation-reduction series, as usually arranged, commences with those reagents which have the greatest negative potentials, and proceeds through the neutral stage to the most positive agents. Any substance in the table will clearly act as a reducing agent towards those which follow it. The following values of potentials of reducing and oxidising agents are valid only for the experimental conditions under which they were determined. The potential differences with reference to the normal hydrogen electrode, using platinum poles, are as follows, the solutions being approximately 0.2 molar:

$SnCl_2$ in KOH	−0.861 volt		$K_2Cr_2O_7$	+0.502 volt	
Na_2S	−0.651 „		KNO_3	+0.577 „	
Hydroxylamine in KOH	−0.616 „		Cl_2 in KOH	+0.626 „	
I_2 in KI	−0.328 „		$FeCl_3$	+0.678 „	
Hydrogen in HCl	−0.311 „		HNO_3	+0.697 „	
I_2 in KOH	−0.070 „		$HClO_4$	+0.707 „	
$SnCl_2$ in HCl	−0.064 „		$H_2Cr_2O_7$	+0.837 „	
NaH_2PO_2	−0.044 „		$HClO_3$	+0.856 „	
$CuCl_2$	+0.000 „		Br_2 in KBr	+0.805 „	
$FeSO_4$ neutr.	+0.073 „		KIO_3	+0.929 „	
Hydroxylamine	+0.076 „		MnO_2 in KCl	+1.068 „	
H_2SO_3	+0.158 „		Cl_2 in KCl	+1.106 „	
$FeSO_4$ in H_2SO_4	+0.234 „		$KMnO_4$	+1.203 „	

The table shows that the oxidising power of reagents is a relative property. The oxidising powers of the same reagent are not constant, but are greatly influenced by the nature of the solvent; e.g. chlorine is a very much stronger oxidising agent in potassium chloride solution than when dissolved in alkalis, while the reducing properties of stannous chloride are weaker in acid than in alkaline solution.

The theory of the preparation of the halogens by the displacement method is made plain by the foregoing treatment of oxidation. The formation of the free elements from their ions will first be discussed.

The facility with which ions are discharged increases with diminution in the electro-affinity of the atoms concerned; of the halogen group, iodine is the most readily liberated by this method, fluorine with the greatest difficulty. The halogen ions can be discharged by all substances having a stronger affinity for electrons.

Preparation of Fluorine.—Fluorine cannot be liberated from its ions by the double decomposition method, since it is the most electronegative of all the elements. Electrolytic methods are therefore used. The electrolysis must obviously be carried out in a medium which has no chemical action on fluorine. Water must not be employed, since the hydroxyl ions give up their negative charges, and ozonised oxygen is evolved instead of the halogen: $F + OH' \longrightarrow F' + H' + O$.

Fluorine is best prepared by electrolysis of anhydrous hydrofluoric acid or fused fluorides, e.g. KHF_2, KH_3F_4, CsH_2F_3. The liquid acts as its own solvent, and the fluoride is partly dissociated into its ions.

As the fluorine ions are discharged by the current, equilibrium is maintained by the dissociation of further quantities of hydrofluoric acid; this process continues until the electrolysis is complete, although the initial fraction of acid which was dissociated may have been very small. Pure hydrofluoric acid is not employed in the preparation, because, like pure water, it is scarcely dissociated and is therefore almost a non-conductor of electricity. The conductivity of the acid is greatly increased, however, by the addition of soluble fluorides, e.g. potassium or ammonium fluorides, just as pure water becomes a good electrolyte by dissolving in it small quantities of salts.

The vessel in which the electrolysis is carried out and the exit tubes must be made of some material not attacked, or attacked only superficially, by fluorine; platinum, copper, silver, magnesium, Monel-metal, nickel or graphite are suitable for the purpose; pure graphite can be used as electrodes. The retention of the very volatile hydrofluoric acid, which otherwise escapes with the fluorine, is effected if the electrolyte remains liquid at low temperatures, by surrounding the apparatus with a bath of boiling methyl chloride (b.pt. $-23°$) or a mixture of solid carbon dioxide and alcohol. The fluorine is scrubbed with solid sodium fluoride to remove the last traces of hydrofluoric acid.[1]

[1] *Cf.* Henne, *J. Amer. Chem. Soc.,* 1938, 60, 6096.

Preparation of Chlorine.—The ions of chlorine, bromine and iodine can be discharged by purely chemical means. The affinity of the halogens for electrons decreases with rise in atomic weight; and hence iodide ions are discharged by atoms of bromine, chlorine or fluorine; bromide ions by chlorine or fluorine; and chloride ions by fluorine.

The halogens can also be displaced by oxygen at high temperatures. The Deacon process for the manufacture of chlorine was based upon the displacement of chlorine from hydrochloric acid by oxygen: $4HCl + O_2 \rightleftharpoons 2H_2O + 2Cl_2$. The conditions of equilibrium have been thoroughly investigated. At 600° the yield of chlorine is 50 per cent. The affinity of oxygen for hydrogen increases more rapidly than that of chlorine as the temperature falls, and so better yields of halogen are obtained at lower temperatures; under these conditions, however, the reaction proceeds much more slowly, and the lowest temperature employed in practice is 400°, corresponding to a yield of 80 per cent. of chlorine. The catalytic influence of $CuCl_2$ upon the reaction was discovered by Deacon; other copper salts, including the sulphate, or nickel and manganous salts, may be used as catalysts, but are not so efficient as cupric chloride. Deacon explained the action of the copper chloride as follows: the cupric salt decomposes into cuprous chloride and chlorine, $2CuCl_2 \longrightarrow 2CuCl + Cl_2$; basic salt is then formed by the action of oxygen on the cuprous chloride, and probably has the composition $CuO \cdot CuCl_2$; finally, cupric chloride is re-formed by interaction of this compound with hydrochloric acid. This scheme of changes is fundamentally correct, but is not a complete explanation of the part played by the catalyst.

Other chlorine compounds besides hydrochloric acid are decomposed by oxygen. The reaction with magnesium chloride has become of technical importance, owing to the production of large quantities of this salt as a by-product of chemical industry. The oxidation of magnesium chloride is also a reversible change:

$$MgCl_2 + \tfrac{1}{2}O_2 \rightleftharpoons MgO + Cl_2.$$
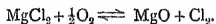
The yield of free chlorine is 50 per cent. at 750°. The formation of an intermediate oxychloride permits of the substitution of magnesium chloride for cupric chloride as contact catalyst in the Deacon process.

The liberation of chlorine from hydrochloric acid by wet processes requires the use of stronger oxidising agents such as permanganic acid, $HMnO_4$, chromic acid, H_2CrO_4, or oxyacids of chlorine, $HClO$ and $HClO_3$. Oxidation of HCl by these reagents takes place only in acid solution; this behaviour is perhaps explained by differences in the constitutions of the free acids and their salts (pp. 360-361); previous examples of the influence of solvent upon the oxidation potential of the same reagent have been given.

The rapid evolution of chlorine produced from a mixture of hydro-

chloric and hypochlorous acids can be interpreted as a decomposition method of preparation. The method may be modified by treating bleaching powder, which has been compressed into cubes, with acid in a Kipp's apparatus: $CaOCl_2 + 2HCl \longrightarrow CaCl_2 + H_2O + Cl_2$. It is probable that the reaction involves the formation of an intermediate addition compound of the oxygen with the HCl; the hypothesis agrees well with Schäfer's auxiliary valency formula for hypochlorous acid [1]:

$$\begin{array}{c}
\text{Cl} \\
| \quad \searrow \text{O} \\
\text{H} \nearrow
\end{array}
+
\begin{array}{c}
\text{Cl} \\
|
\\
\text{H}
\end{array}
\longrightarrow
\begin{array}{c}
\text{Cl} \searrow \quad \nearrow \text{Cl} \\
| \quad \searrow \text{O} \searrow \\
\text{H} \nearrow \qquad \text{H}
\end{array}
\longrightarrow
\begin{array}{c}
\text{Cl} \text{---} \text{Cl} \\
+ \\
\text{H} \text{---} \text{O} \text{---} \text{H}
\end{array}$$
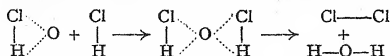
This assumption of an intermediate addition compound affords an explanation of the superiority of hypochlorous acid as an oxidising agent compared with the higher oxyacids of chlorine. Two chlorine atoms are attached to each oxygen atom in the molecules of the compound $HClO \cdot HCl$, while in the complex $HClO_3 \cdot 3HCl$ the quantity of chlorine attached to an oxygen atom is only the equivalent of 1·33 atoms; hence the chloric acid derivative is likely to be more stable than that of hypochlorous acid.

Electrolytic methods are of great importance in the manufacture of chlorine, and have now largely superseded the purely chemical processes. Actually, chlorine is obtained as a valuable by-product of the electrolysis of alkali chlorides. The description of the process is therefore included in the discussion of the main products of electrolysis (see pp. 191, 414).

Preparation of Bromine.—The methods by which bromine is obtained are analogous to those used for chlorine, but oxidising agents, other than those available for the production of chlorine, liberate bromine from its compounds. These include various reagents which do not as a rule behave as oxidising agents, *e.g.* concentrated sulphuric acid as well as chlorine itself, which is almost exclusively used in the isolation of bromine on the large scale from $MgBr_2$ and from the bromides in sea water; the latter is kept at pH 3—4 by addition of sulphuric acid to prevent reaction of the liberated bromine with the water.

Before the production of chlorine by electrolysis reached its present dimensions the amount of the element available for chemical purposes was limited, and much bromine was then also obtained electrolytically from the carnallite mother liquors. It was possible to separate bromine from chlorine by this method, since the decomposition voltage of bromides is lower than that of chlorides:

Decomposition potentials of chlorides, bromides and iodides

		Cl	Br	I
Na	. . .	1·77	1·49	·95 volt
H	. . .	1·36	1·08	·54 „

[1] *Z. physikal. Chem.*, 1919, **93**, 318.

The potential differences of the free halogens in contact with normal solutions at 25° are :

I_2/N . KI	.	. 0·566 volt		Cl_2/N . HCl .	. .	1·366 volt
Br_2/N . KBr	.	. 1·121 ,,		F_2/N . HF .	. .	1·85 ,,

The employment of an intermediate voltage therefore resulted in the complete liberation of bromine, while the whole of the chlorine was left in the ionic state in solution. The anode was made of carbon or pyrolusite and a cathode chosen which was not polarised. The electrolysis was carried out without any diaphragm, since the small quantities of hypobromites formed at the cathode were reduced back to bromide.

Preparation of Iodine.—Iodine is obtained very easily from its compounds, sometimes without the use of reagents. The oxidation of iodine compounds proceeds much more readily in acid than in neutral solution, because H˙ ions accelerate the discharge of I′ ions catalytically. The presence of large quantities of undissociated hydrogen iodide in the more concentrated solutions also favours the liberation of iodine, since the free acid, being strongly endothermic, is more readily attacked by the oxidising agent than the iodide ions or the exothermic metallic iodides. This method of preparation involves both decomposition and substitution, but consists chiefly of the latter process.

Oxygen easily displaces iodine from hydriodic acid ; the reaction is slow at room temperature, but proceeds rapidly at higher temperatures. A mixture of the two gases is inflammable, and burns with a red flame. Compounds able to liberate nascent oxygen act more vigorously than molecular oxygen. Hydrogen peroxide is a good example, but even this reagent does not cause the instantaneous liberation of iodine, and the reaction must not be regarded as simple ionic substitution.

The reaction with H_2O_2 proceeds quite differently in acidic and neutral solutions ; in the presence of acid it takes place in two stages.[1] First there is a fairly slow change : $H_2O_2 + I' \longrightarrow H_2O + IO'$, which is at once followed by the practically instantaneous reaction $IO' + 2H˙ + I' \longrightarrow H_2O + I_2$. The quantity of iodine set free in neutral solution, on the other hand, is very small ; the halogen mainly plays the part of a catalyst for the decomposition of H_2O_2, and consequently oxygen is evolved.

The reaction between H_2O_2 and HI is very much accelerated by addition of a little molybdic acid. Probably a permolybdic acid is formed as an intermediate product, which loses oxygen more readily than hydrogen peroxide. The production, by the action of H_2O_2 on molybdates, of permolybdates which attack hydrogen iodide supports this explanation. Other per-acids behave similarly. Caro's acid, H_2SO_5, for example, readily liberates iodine from hydrogen iodide, but the reaction with perdisulphuric acid, $H_2S_2O_8$ is much slower, and

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[1] Noyes and Scott, *Z. physikal. Chem.*, 1895, **18**, 118 ; 1896, **19**, 692.

the liberation of halogen is probably preceded by the hydrolysis of $H_2S_2O_8$ with the formation of Caro's acid.

The endothermic oxides of nitrogen oxidise hydriodic acid to iodine or even to a further stage. Nitric and nitrous oxides are slowly reduced to ammonia when treated with HI; the action of nitrous acid upon the hydracid, however, is more vigorous, and pure nitric oxide is at first evolved: $HNO_2 + HI \longrightarrow NO + I + H_2O$. With nitric acid the reaction is so vigorous that the mixture sometimes ignites, burning with a red flame.

Iodine is also liberated when iodides are treated with sulphur trioxide or concentrated sulphuric acid; sulphur dioxide, sulphur or even hydrogen sulphide are found among the products of the action, the extent of reduction depending on the conditions under which the experiment is conducted. Even free sulphur itself can displace iodine from hydrogen iodide by combining with the hydrogen to form hydrogen sulphide. The reaction takes place either in the presence or absence of water, but proceeds much more rapidly in aqueous solution. The chemical change, which is reversible, is represented by the equation $2HI + S \rightleftharpoons H_2S + I_2$. The position of equilibrium, under normal conditions, is greatly in favour of the action expressed by the lower arrow. Phosphorus pentoxide is not attacked by HI, but $POCl_3$ reacts with hydrogen iodide at a high temperature with the production of iodine and PCl_3.

The iodine in hydriodic acid is easily replaced by the other halogens. Compounds of the halogens may be utilised for this purpose as well as the free elements. Thus sulphur chloride, S_2Cl_2, reacts vigorously with hydrogen iodide with the production of I_2, HCl and H_2S. The iodine in hydrogen iodide is also set free by sulphuryl chloride, SO_2Cl_2.

Iodine is not necessarily obtained in the free state by the decomposition of hydrogen iodide, for it may combine with the liberating reagent. For instance, the decomposition of hydrogen iodide with phosphorus gives PI_3. When iodine ions are brought in contact with hypochlorites or chlorites, part of the iodine is set free and part is oxidised to iodate.

All reagents which oxidise hydrogen chloride, e.g. chloric acid, chromic acid and permanganic acid, are, of course, able to liberate iodine from hydrogen iodide, as this compound is more readily oxidised than its chlorine analogue. These reactions are quantitative and can be used for estimation of the oxidising agent by titration of the iodine with thiosulphate. Iodic acid is readily reduced by hydrogen iodide and other reagents to free iodine. The commercial preparation of iodine is based upon this property. In Chile, the sodium iodate present in the saltpetre mother liquors is reduced to iodine by treatment with a mixture of acid and neutral sulphite:

$$2NaIO_3 + 3Na_2SO_3 + 2NaHSO_3 \longrightarrow 5Na_2SO_4 + I_2 + H_2O.$$
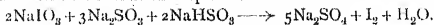
The reduction of arsenic acid by iodides is used for the volumetric estimation of arsenic, or for the standardisation of iodine solution. The reaction is complete only in strongly acid solutions [1] :

$$H_3AsO_4 + 2I' + 2H^{\boldsymbol{\cdot}} \rightleftharpoons H_3AsO_3 + I_2 + H_2O.$$
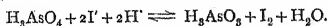
The oxidation of arsenites to arsenates by iodine becomes quantitative in the presence of sufficient bicarbonate to neutralise the hydriodic acid as fast as it is formed.

Preparation of "Pseudo-Halogens"

The free radicals cyanogen $(CN)_2$ oxy-, thio- and seleno-cyanogen $(CNO)_2$, $(CNS)_2$ $(CNSe)_2$ resemble the halogens in many properties, e.g. in smell, in liberation of I_2 from KI, and in dissolving metals without evolution of hydrogen. It is therefore convenient to indicate here the methods by which they may be prepared.

Cyanogen is formed by the thermal decomposition of cyanides of the noble metals: $2AgCN \longrightarrow 2Ag + (CN)_2$; $Hg(CN)_2 \longrightarrow Hg + (CN)_2$. The decomposition of mercuric cyanide proceeds at a lower temperature if it is mixed with mercuric chloride: $Hg(CN)_2 + HgCl_2 \longrightarrow Hg_2Cl_2 + (CN)_2$. A less pure product is obtained when warm solutions of $CuSO_4$ and KCN are mixed :

$$CuSO_4 + 2KCN \longrightarrow Cu(CN)_2 + K_2SO_4$$
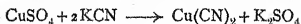
the yellow precipitate of $Cu(CN)_2$ decomposing rapidly :

$$2Cu(CN)_2 \longrightarrow 2CuCN + (CN)_2.$$
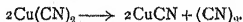
Oxycyanogen $(CNO)_2$ results as colourless crystals (m.pt. about $-12°$) from the interaction [2] of AgCNO and I_2 in CCl_4 or CS_2 solution. It was obtained in solution by the electrolysis [3] of alcoholic KCNO solution. The same authors prepared $(CNSe)_2$ as a yellow powder from AgCNSe and I_2 in organic solvents, while Söderbäck [4] obtained $(CNS)_2$, m.pt. $-3°$, from $Pb(CNS)_2$ and Br_2 in dry ethereal solution ; other thiocyanates behave similarly but the reaction with iodine is less satisfactory.

Preparation of Oxygen

Oxygen is manufactured on the large scale from liquid air, which is obtained by a system of cumulative cooling. Compressed air is cooled by allowing it to expand suddenly, and this chilled air is then utilised in its return to the compression pumps to cool the oncoming air ; the fresh air undergoes a similar expansion with production of a still lower temperature. Eventually, the original air returns to the

[1] Roebuck, J. Phys. Chem., 1902, 6, 365.
[2] H. Hunt, J. Amer. Chem. Soc., 1932, 54, 907.
[3] Birckenbach and Kellermann, Ber., 1925, 58 [B], 786.
[4] Ann., 1919, 419, 217.

expansion orifice to be further chilled. The cycle is repeated many times until finally the temperature of the air falls so low that liquefaction occurs (Linde). The various components of the liquid air are then separated by fractional distillation. The more volatile nitrogen (b.pt. $-195 \cdot 7°$) boils off before the oxygen, which has b.pt. $-183°$. On further evaporation, the whole of the oxygen escapes, leaving behind liquid carbon dioxide and water if these are not previously removed. The oxygen is finally purified by recondensing the impure gas and repeating the fractional evaporation several times; even then it contains some argon (b.pt. $-186 \cdot 1°$).

1. DISPLACEMENT METHODS

The element is obtained electrolytically by the discharge of oxygen or hydroxyl ions. Water containing a little sulphuric acid (or, on the large scale, sodium hydroxide) to improve its conductivity is used as the electrolyte. Electrolysis occurs with evolution of oxygen from an unpolarisable anode, provided the applied E.M.F. exceeds the decomposition voltage of the solution.

Fluorine is the only element which is sufficiently electronegative to bring about the instantaneous discharge of oxygen ions. The action of fluorine on water is expressed by the equation: $F_2 + H_2{}^{··}O'' \longrightarrow 2H^·F' + O$ (ozonised oxygen).

Chlorine can displace oxygen slowly from water, especially in sunlight; hypochlorous acid is formed as an intermediate product (see p. 363):

I. $Cl_2 + H_2O \longrightarrow HClO + HCl$.   II. $HClO \longrightarrow HCl + O$.
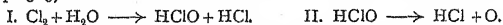
This method cannot strictly be classed as one of substitution, for the second stage of the reaction involves a decomposition.

Owing to the great affinity of most of the elements for oxygen, the latter is never set free by treatment of its compounds with elements other than fluorine, chlorine and bromine, but enters into combination with them. Thus the reaction between sulphur and metallic oxides does not result in the formation of sulphide and oxygen, but of sulphide and sulphur dioxide: $2MO + 3S \longrightarrow 2MS + SO_2$. Even chlorine unites with oxygen when mercuric oxide is treated with the halogen: $HgO + 2Cl_2 \longrightarrow HgCl_2 + Cl_2O$. Oxygen is liberated from metallic oxides only by fluorine.

2. DECOMPOSITION METHODS

The affinity of elements for oxygen is approximately proportional to their tendency to form positively charged ions (see also pp. 151, 441). Hence oxides of non-metals and of the less electropositive metals are generally decomposed with ease. Those of chlorine are very liable to explode. The compounds of the noble metals give off oxygen at a comparatively low temperature, and are reduced to the metallic state. Metals which recombine with oxygen on cooling can be utilised for the

preparation of oxygen from the air. Lavoisier's classical researches on oxygen, in which he converted mercury into the red oxide by the action of heat, and then decomposed the latter at a higher temperature, depend upon this principle.

The lower oxides of the more electropositive metals are not completely decomposed by heat; if the metal forms several compounds with oxygen the higher oxides give off part of their oxygen when heated and are converted into the lower oxides (cf. pp. 443-447). An increase in the number of atoms of the second element attached to a central atom, which occurs during the formation of higher oxides, usually involves a decrease in stability of the compound. The oxides of manganese afford a good illustration of this point; the monoxide, MnO, is so stable that it can be heated in any ordinary furnace without decomposition; the second oxygen atom in MnO_2 is removed without difficulty by the action of heat, while the higher oxides, such as Mn_2O_7, after a preliminary warming to start the decomposition, give off oxygen spontaneously. Manganese dioxide (pyrolusite), which is fairly cheap, may be used for the preparation of small quantities of oxygen, although the temperature required for the evolution of oxygen is somewhat high. Lead dioxide, PbO_2, is more costly than pyrolusite, but gives off oxygen at a lower temperature, and is easily converted into PbO over the Bunsen burner. The compound with calcium oxide, calcium plumbate, is also decomposed by heat, though not quite so easily as PbO_2 itself, with production of PbO and CaO. The monoxide, moreover, absorbs oxygen on cooling, or when subjected to a higher pressure, with regeneration of the plumbate. A mixture of PbO and CaO can thus be employed for the separation of oxygen from nitrogen in the air by alternately lowering and raising the pressure; the oxygen is absorbed at the higher pressure (the nitrogen being simultaneously swept out of the reaction zone) and recovered as the pressure falls. Kassner attempted to adapt this process to the large-scale preparation of oxygen. Ferric oxide is not a convenient source of oxygen owing to its high decomposition temperature. BaO_2, which is transformed into BaO by the action of heat, is a particularly suitable material for the production of oxygen. This reaction is reversible, like the decomposition of calcium plumbate: $2BaO_2 \rightleftarrows 2BaO + O_2$, and has been utilised for the manufacture of oxygen (Brin's process—now obsolete).

The peroxides of the alkali metals (Na_2O_2, KO_2) do not form the typical monoxides (Na_2O, K_2O) when heated. The highest member of a series of three oxides derived from the same metal is sometimes converted directly into the lowest oxide by the action of heat, even when the operation is carried out cautiously. Some oxides decompose into a higher oxide and the metal: $2PtO \longrightarrow PtO_2 + Pt$.

This type of change occurs when the higher oxide is the more stable compound, and obviously does not involve the liberation of oxygen. Wöhler has observed many examples of this behaviour with metals of the platinum group.[1] If IrO_2 is heated in

¹ Z. Elektrochem., 1907, 15, 129.

an atmosphere of oxygen to a temperature at which the dissociation pressure just exceeds that of the oxygen in the surrounding atmosphere, the decomposition proceeds further than the sesquioxide stage, Ir_2O_3, with the production of the metal. Attempts to prepare Ir_2O_3 from the corresponding hydroxide, which is well known, result in the formation of the metal and IrO_2; hence the oxide in which iridium is tervalent is less stable than the quadrivalent derivative. This simultaneous oxidation and reduction of compounds, in which one element possesses an intermediate valency, is not confined to the oxides (*cf.* Luther's Rule, p. 376).

The higher oxides of many metals possess acidic properties and can combine with other metallic oxides; this salt formation is accompanied by a decrease in the tendency to split off oxygen, so that derivatives of oxides which are too unstable to exist alone can be prepared. As already observed, the compound of PbO_2 with CaO is more stable than PbO_2 itself. The higher oxides of manganese have not been obtained in the pure state, but form the stable manganates and permanganates with bases. Salts have been obtained which are derivatives of an unknown iron trioxide, *e.g.* potassium ferrate, $K_2O . FeO_3$, *i.e.* K_2FeO_4. Chromium trioxide, CrO_3, gives off oxygen fairly readily when warmed, but the corresponding salts, the chromates, are stable towards the action of heat. The formation of salts by oxides of non-metals also involves an increase in the affinity of the molecule for oxygen. Chloric anhydride, Cl_2O_5, is not known, but its salts are moderately stable. Many similar examples might be quoted. To summarise: When an oxide, which easily loses oxygen, forms one component of another compound, the tendency towards reduction is greatly diminished. Other classes of compounds, particularly the halides, exhibit a similar behaviour.

Oxygen can be obtained from compounds other than oxides by the decomposition method. Thus the nitrates of the alkali metals give off part of their oxygen when heated to a moderate temperature, leaving a residue of nitrite: $2KNO_3 \longrightarrow 2KNO_2 + O_2$. Potassium chlorate loses the whole of its oxygen when strongly heated: $2KClO_3 \longrightarrow 2KCl + 3O_2$. The actual decomposition, however, occurs in two stages; potassium perchlorate is formed first as an intermediate product with the simultaneous liberation of part of the oxygen, and then as the temperature is raised the perchlorate decomposes completely into chloride and oxygen. (See also Chap. XIII.) These reactions, in which energy is set free, might be expected to proceed spontaneously, but in practice there are factors which exert a strong retarding effect; this explains the extreme sensitiveness of these decompositions to the influence of catalysts. Manganese dioxide is generally used as catalyst for the potassium chlorate reaction, and perchlorate is not then formed.

Catalysts are substances which alter the velocity of a reaction. A positive catalyst is one which accelerates a chemical change; a negative catalyst is one which diminishes the speed of a reaction. The catalyst supplies no energy to the chemical system, and therefore has no power to start a reaction which involves the absorption of energy. The mechanism of catalysis consists either in a rapid formation and decomposition of a very unstable intermediate product, or it may depend upon a local accumulation of energy in the surface layers of the

reagents, produced, for example, by adsorption, when the resulting intimate contact causes an increase in the rate of chemical change. Catalysts which act in this physical manner are termed surface catalysts. Ostwald has compared the action of positive catalysts with that of a lubricant in accelerating the movement of rusty machinery.

The catalytic influence of manganese dioxide on decompositions which involve the evolution of oxygen is probably due to the transitory formation of a higher oxide of manganese. Derivatives of such an oxide (MnO_3), the manganates, which can be obtained in alkaline solution, are at once decomposed by acidification ; these salts are also produced in neutral solution, but are quickly hydrolysed. The part played by manganese dioxide in the decomposition of potassium nitrate may possibly be represented by the equations :

I. $KNO_3 + MnO_2 \longrightarrow KNO_2 + MnO_3$.   II. $MnO_3 \longrightarrow MnO_2 + O$.
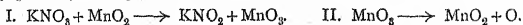
This hypothesis explains why the manganese dioxide is not used up during the reaction.

Hydrogen peroxide, ozone and hypochlorous acid can also be catalytically decomposed at ordinary temperatures with evolution of oxygen. The oxides of silver and mercury, as well as manganese dioxide, act as catalysts for these reactions. Cobalt oxide is a particularly efficient catalyst for the decomposition of hypochlorites ; cobalt is known to form a peroxide in alkaline solution. The addition of a very small quantity of a cobalt salt to a solution of bleaching powder produces a steady evolution of oxygen : $2HOCl \longrightarrow 2HCl + O_2$. The decomposition of hydrogen peroxide by oxyacids ($HOCl$, $HMnO_4$, H_2CrO_4) may involve the transitory formation of per-acids. The oxygen liberated by the decomposition of the blue perchromate solution is derived from the reduction of sexavalent chromium to the tervalent state, as well as from the hydrogen peroxide. Similarly, when permanganate is treated with hydrogen peroxide, oxygen is derived not only from the decomposition of the peroxide, but also from the permanganate (probably after the transitory formation of a per-permanganic acid), which is reduced in consequence to a manganous salt : $2HMnO_4 + 5H_2O_2 \longrightarrow 2MnO + 6H_2O + 5O_2$.

Preparation of Sulphur, Selenium and Tellurium

Large quantities of sulphur occur free in nature. The low melting point of the element facilitates its isolation from mineral matter. Deposits which are rich in free sulphur are treated with steam under pressure and thus the molten sulphur is easily separated. Ores having a smaller sulphur content are stacked in heaps on a sloping floor, the arrangement resembling that of a charcoal pile, and the inside of the pile is ignited. The heat of combustion suffices to melt the whole of the sulphur, which flows away to the bottom of the kiln. This crude

process is very wasteful, since some of the sulphur is used as a fuel, while a still larger portion is consumed in the reduction of gypsum present in the gangue: $CaSO_4 + 2S \longrightarrow CaS + 2SO_2$.

Smaller quantities of sulphur are obtained industrially by decomposition and substitution methods. The element is readily liberated by the former process from polysulphides or free sulphuretted hydrogen. Thus sulphur can be distilled off by heating pyrites, FeS_2, or CaS_x in the dry state; calcium polysulphide was formerly a by-product of the Leblanc soda process. The polysulphides lose the whole of their sulphur in excess of that required to satisfy the typical valency of the metal: thus FeS_2 and CaS_x are converted into FeS and CaS respectively. The separation of sulphur from acidified solutions of polysulphides and thiosulphates is based on the same principles as the dry methods of preparation. The free acids are formed first, but decompose quickly at room temperatures:

$$H_2S_5 \longrightarrow H_2S + 4S \qquad H_2S_2O_3 \longrightarrow H_2SO_3 + S.$$
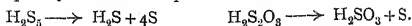
The relatively small affinity of sulphur for hydrogen is illustrated by the ease with which hydrogen sulphide itself can be decomposed. Rise of temperature displaces the equilibrium $H_2S \rightleftharpoons H_2 + S$ in the direction of the upper arrow; at a red-heat, about 7 per cent. of the hydrogen sulphide is dissociated; above 1600° the decomposition is almost complete.

Sulphur is also readily obtained from sulphuretted hydrogen by the displacement method. The sulphur in H_2S is replaced by oxygen by the action of such weak oxidising agents as sulphurous acid or concentrated sulphuric acid:

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S \qquad 3H_2S + SO_3 \longrightarrow 3H_2O + 4S.$$

The displacement is of course more rapid when stronger oxidising agents are employed, e.g. the halogens or nitric acid. The sulphur recovery process of Chance and Claus makes use of the oxygen of the air in the presence of a contact catalyst, Fe_2O_3, and is of technical importance. The process is very efficient, the loss of sulphur by ignition being negligible.

Sulphur dioxide is quantitatively and rapidly decomposed by coke at 1100° according to the exothermic reaction $SO_2 + C = CO_2 + S$ and the process is used for the recovery of sulphur from flue-gases.[1]

Sulphur dioxide in the flue-gases is first absorbed in a buffered sulphite-bisulphite solution containing aluminium chloride; if this solution is heated its pH diminishes,[2] with consequent liberation of SO_2, which then can be reduced as above.

The methods for the preparation of selenium and tellurium are very similar in theory to those used for the production of sulphur.

[1] Appleby, *Chem. and Ind.*, 1934, **53**, 1097.
[2] The pH of a solution is the logarithm to base 10 of the reciprocal of the hydrogen ion concentration in the solution.

The chief source of these elements is the anode mud formed during the electrolytic refining of copper (p. 204). Most of the Se is volatilised as SeO_2 on roasting the mud in air. The residual Se and Te are extracted as water-soluble selenite and tellurite after fusion of the mud with saltpetre and sodium hydroxide. On acidifying, TeO_2 is precipitated and Se is obtained from the mother liquor, as it is from the hydrochloric acid solution of the volatilised SeO_2, by reduction with SO_2. The tellurium is liberated from the TeO_2 by charcoal reduction or by SO_2 reduction of a hydrochloric acid solution.

Other sources of selenium are the mineral zorgite, a double selenide of lead and copper, and the residue from the lead chambers used in sulphuric acid manufacture, which consists principally of lead sulphate, but also contains uncombined selenium. The latter can be extracted from the residue by potassium cyanide as the selenium analogue of thiocyanate:

$$KCN + S \longrightarrow KCNS \qquad KCN + Se \longrightarrow KCNSe.$$

The two compounds, however, behave differently when their solutions are acidified; the liberated acid, HCNS, remains undecomposed in solution, while the free acid, HCNSe, breaks up immediately with the precipitation of selenium. In general, selenium is liberated from its compounds more easily than sulphur from the corresponding derivatives. The alkali selenides, for example, are very readily oxidised and this property can be applied to the preparation of the element from seleniferous mud; the solution of Na_2Se obtained by treatment with caustic soda deposits selenium on standing in the air. The selenium compounds can be reduced with exceptional ease, and their tendency to decompose with liberation of the element is a very characteristic property. Thus selenium is re-precipitated from an *aqua regia* solution in which it is present as SeO_2, by passing a stream of sulphur dioxide through the liquid: $SeO_2 + 2SO_2 \longrightarrow Se + 2SO_3$; the element can also be isolated in the dry way by roasting with ammonium chloride the residue left after evaporation of the original solution.

Another method for the preparation of tellurium consists in converting bismuth telluride into Na_2Te, the solution being then oxidised by exposure to the air. Tellurium ores may also be dissolved in *aqua regia* or concentrated sulphuric acid; the element is then precipitated from the solution of tellurous acid thus obtained by a stream of sulphur dioxide, or by addition of a base metal.

Preparation of Nitrogen

Nitrogen is generally prepared on the large scale from liquid air (see p. 170). This process allows of the complete removal of the rare gases, some of which are more volatile and some less volatile than the

nitrogen. The oxygen of the air can also be removed either by absorption with alkaline pyrogallol, ferrous salts, etc., or, in the dry way, by causing it to combine with phosphorus at a low temperature, or with strongly heated copper.

Nitrogen can be obtained from its compounds either by decomposition or substitution methods. The compounds of many of the non-metals with nitrogen, especially those of sulphur and the halogens, are endothermic and tend to decompose into their elements. The formation of ammonia is exothermic, and the equilibrium of the reversible change: $N_2 + 3H_2 \rightleftharpoons 2NH_3$, is displaced in favour of the formation of free nitrogen as the temperature rises. The decomposition of hydrazine, N_2H_4, takes place more readily than that of ammonia (in the presence of catalysts, at room temperature), and is an irreversible reaction. Nitrogen is also produced, together with some ammonia and oxides of nitrogen, by the decomposition of hydroxylamine; it is possibly formed by a secondary reaction. Hydrazoic acid, nitrogen chloride and nitrogen iodide are very unstable and decompose into their constituent elements, sometimes with explosive violence. Iodine azide, N_3I (see p. 663), either in the solid state or in non-aqueous solutions, gradually decomposes into nitrogen and iodine. Metal azides decompose slowly when gently warmed, nitrogen is given off and the metal left. The cautious decomposition of these salts affords a good method of obtaining nitrogen in a high state of purity, as there is no possibility of contamination with other gaseous products. Nitrogen is also set free by exploding the sulphides N_4S_4 and N_2S_5, although these methods are of course unsuitable for the preparation of the gas.

Nitrogen is also evolved on heating organic diazo-compounds, e.g. $C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2$. Certain aliphatic diazo-derivatives, e.g. diazoacetic ester, also decompose with evolution of nitrogen; the reaction, judging by the final products, appears to be a kind of hydrolysis:

$$N_2CH . CO_2C_2H_5 + H_2O \longrightarrow N_2 + CH_2(OH) CO_2C_2H_5.$$
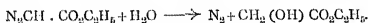
Finally, nitrogen is obtained by the action of heat or the electric discharge on nitrous oxide, but the gas which results from the decomposition of the higher oxides is impure.

The *displacement* methods of preparing nitrogen include the action of ammonia on the halogens: $2NH_3 + 3Cl_2 \longrightarrow N_2 + 6HCl$. This reaction takes place in stages; nitrogen halides are first formed, and then undergo double decomposition with the excess of ammonia: $NCl_3 + NH_3 \longrightarrow N_2 + 3HCl$. It is preferable to use hypochlorites or hypobromites in place of free halogens. A regular stream of nitrogen can be obtained in a Kipp's apparatus by the interaction of strong ammonia and compressed cubes of bleaching powder. The reaction with hypobromites proceeds very smoothly and has been utilised for

the quantitative estimation of nitrogen in ammonium compounds.   The complete reaction is

$$3NaOBr + 2NH_3 \longrightarrow 3NaBr + N_2 + 3H_2O.$$
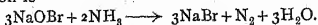
Here again halogen derivatives of ammonia are formed as intermediate products.

There is no appreciable reaction between nitrous oxide and ammonia at room temperature, but the mixture explodes when heated, the oxygen of the nitrous oxide uniting with the hydrogen of the ammonia just as, in the reaction described above, the chlorine of nitrogen chloride combines with it.   Nitric oxide acts on ammonia less vigorously than nitrous oxide, and nitrogen is liberated only at high temperatures. The interaction of ammonia and nitrous acid is of special interest. An aqueous solution of ammonium nitrite, or a mixture of NH_4X and MNO_2, say NH_4Cl and $NaNO_2$, readily decomposes according to the equation $NH_4NO_2 \longrightarrow N_2 + 2H_2O$.   The chemical change is intramolecular, one part of the molecule being oxidised and the other part reduced.   Nitrogen results from both the oxidising and reducing actions, and hence the complete change appears to be one of direct decomposition.

The real nature of this reaction is more obvious when substituted ammonias react with nitrous acid, for the process then comes to a standstill at an intermediate stage without evolution of nitrogen. This product is a diazo-compound and is itself decomposed more or less easily to give free nitrogen. In the aliphatic series the diazo-compounds are so unstable that they are difficult to isolate.

The conversion of ammonia into nitrogen is an oxidation process. Nitrogen is therefore liberated by the action of numerous oxidising agents, including oxygen itself, upon ammonia.   A mixture of the two gases burns when ignited, with the production of nitrogen. The oxidation of ammonia is still more violent when very strong oxidising agents are used, particularly if the ammonia is already in a state of combination with the oxidiser, as in ammonium nitrite.   Another suitable compound is ammonium dichromate: $(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$.   The reaction, started by bringing a red-hot wire in contact with the solid, spreads slowly throughout the whole mass, which finally glows and is converted into a bulky residue approximating to Cr_2O_3.   Ammonium nitrate, when heated, may decompose violently and may even explode.   The chlorate is still more liable to explode; the ammonium group is here oxidised at the expense of the oxygen of the chlorate radical.   Addition compounds of the heavy metal chlorates, e.g. $Ni(ClO_3)_2 \cdot 6NH_3$, explode violently when struck. The liberation of nitrogen from these also results from intramolecular change involving oxidation-reduction.

Finally, it must be mentioned that nitrogenous compounds are decomposed with production of the free element by the action of certain bacteria and ferments.   The mechanism of these processes is very obscure.

Preparation of Phosphorus

The phosphates are the sole source of elementary phosphorus. The principle of the preparation consists in the reduction of phosphoric oxide.

The reduction of normal phosphates with carbon gives a very poor yield of phosphorus, partly owing to the simultaneous formation of carbide[1]: $Ca_3(PO_4)_2 + 14C \longrightarrow 3CaC_2 + 2P + 8CO$. The final product contains a large quantity of calcium phosphide: $Ca_3(PO_4)_2 \longrightarrow Ca_3P_2 + 4O_2$.

Free phosphorus pentoxide is much more easily reduced to phosphorus. The metaphosphates which are obtained by the dehydration of dihydrogen ortho-phosphates lose phosphoric anhydride when strongly ignited :

$$3Ca(H_2PO_4)_2 \longrightarrow 3Ca(PO_3)_2 + 6H_2O \qquad 3Ca(PO_3)_2 \longrightarrow 2P_2O_5 + Ca_3(PO_4)_2.$$

The first step in the production of phosphorus consists in converting the normal phosphate into the dihydrogen salt by the action of concentrated sulphuric acid; the latter salt is then transformed into the metaphosphate by heating to redness. Finally, two-thirds of the phosphoric anhydride contained in the meta-salt is reduced to phosphorus by heating with carbon at a high temperature. The bulk of the remaining phosphorus is reconverted into the normal phosphate, which may then be used over again; a part is reduced also in the manner described above.

A more efficient and practical method consists in heating a mixture of the normal phosphate with an acid anhydride which is less volatile than phosphorus pentoxide, e.g. silica. By such a process the whole of the pentoxide in combination with the base is displaced by the silica. When a mixture of the phosphate and sand is heated to a high temperature, the SiO_2 unites with the CaO. Since the liberated P_2O_5 volatilises as fast as it is formed, it is not able to compete with the silica for the base, and the equilibrium $Ca_3(PO_4)_2 \rightleftharpoons 3CaO + P_2O_5$ is continually displaced in the direction of the upper arrow until finally the whole of the phosphate is converted into calcium silicate. The phosphorus pent-oxide, at the temperature at which it is formed, is readily reduced to phosphorus by carbon. The preparation of phosphorus therefore involves: (1) The displacement of phosphoric anhydride from its salts by means of silica; (2) the reduction of the anhydride with carbon, which may either be carried out simultaneously with the first reaction or as a subsequent process. The complete chemical change is represented by the equation

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow 6CaSiO_3 + 10CO + P_4.$$
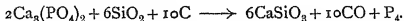
The reaction is preferably conducted in an electric furnace, since the decomposition of the $Ca_3(PO_4)_2$ requires a high temperature. The process used in the large-scale manufacture of phosphorus is a continuous one: the molten slag containing the calcium silicate is periodically run off from the bottom of the furnace and a new charge introduced at the top.

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[1] Hilbert and Frank, *DRP.*, 1895, 92838.

The phosphates of the heavy metals dissociate more readily than calcium phosphate. It has therefore been proposed to convert the calcium salt first of all into lead phosphate from which the phosphorus could be obtained at a comparatively low temperature. Another suggested modification is the use of metals as reducing agents instead of carbon: $6NaPO_3 + 10Al + 3SiO_2 \longrightarrow 3Na_2SiO_3 + 5Al_2O_3 + 6P$. These methods, however, have not become of technical importance.

Bone ash was originally used as the starting material in the production of phosphorus, but recently mineral phosphates have also been utilised; e.g. phosphorite, and an aluminium phosphate, Rhedonda phosphate. Basic slag cannot be used, because the iron which it contains causes the formation of an iron phosphide, Fe_3P_2. The addition of a little slag to the bone ash has the advantage that fusion takes place at a lower temperature, and consequently the process is more economical.

Preparation of Boron, Silicon and Titanium

The similarity in the methods for preparing boron and silicon arises from their almost identical affinities for the other elements in the compounds from which they are extracted, as well as from the general resemblance of their chemical properties. The following table gives the heats of formation of the compounds of boron and silicon with equivalent quantities of a few non-metallic elements:

	O	Cl	Br
Si	47·8	30·5	17·8 Cal.
B	45·5	31·1	14·4 ,,

The oxides and allied derivatives are the most important source of elementary boron and silicon. The affinity of these two elements for oxygen is greater than that of all other non-metals, and is only exceeded by that of the alkali and alkaline earth metals and by aluminium. This strong attraction for oxygen influences the methods by which boron and silicon are isolated.

Decomposition methods of preparation have a very restricted application owing to the great chemical affinity of boron and silicon for other elements. A process for the isolation of boron, which consists in heating boron bromide in a high tension arc, has been devised. This method gives a very pure product.[1] The silicon which is liberated as a by-product in the Acheson process for the manufacture of graphite results from the decomposition of carborundum, SiC, into its elements at a very high temperature (2200°-2240°). The carbon residue retains the crystalline structure of the carborundum, while the silicon, which volatilises, is deposited as a sublimate on the interior parts of the furnace; any silicon vapour coming in contact with the air burns to SiO_2. Silicon

[1] R. Meyer and Zappner, *Ber.*, 1921, 54, 550.

is also obtained by the direct decomposition of its hydrogen compounds either by the action of heat or by sparking them. The formation of boron by analogous methods presents greater difficulties. For example, boron carbide, B_6C, is even more stable than SiC, and withstands a temperature of 2800° without decomposition.

These elements are usually prepared by *displacement* methods. As boron and silicon compounds are strongly exothermal, only chemically active elements are useful for this purpose: *e.g.* the alkali and alkaline earth metals, magnesium, aluminium and carbon; phosphorus also displaces boron from its compounds. The reaction of boron and silicon oxides with carbon is, however, accompanied by absorption of heat and thus can be effected only at very high temperatures.

Silicon is obtained more easily from weakly exothermic or endo-thermic derivatives. Silane, which is slightly endothermic, burns readily when ignited in the air, forming free silicon; an amorphous deposit of the element is produced by allowing the flame of the burning gas to impinge on a cold surface. Silicon is made on the large scale by reduction of silica with coke. An excess of silica must be used to prevent the formation of carborundum, which is the first product: $2SiC + SiO_2 \longrightarrow 3Si + 2CO$. Calcium carbide can be used as a reducing agent in place of silicon carbide: $3SiO_2 + 2CaC_2 \longrightarrow 3Si + 2CaO + 4CO$.

The alkali and alkaline earth metals and aluminium reduce silica more easily than carbon, since the affinity of these elements for oxygen is greater. These reactions, once started, proceed to completion accompanied by evolution of heat. Thus if a mixture of powdered magnesium and sand is heated to redness in one spot with a small flame, the reaction spreads throughout the entire mass, which soon becomes incandescent: $SiO_2 + 2Mg \longrightarrow Si + 2MgO$. When sodium is used as the reducing agent, alkali silicates are more suitable than free silica as the source of silicon. In practice it is usual to electrolyse a solution of silica in a mixture of fused sodium and potassium fluorides. The alkali metals set free by the current at once reduce the silica to silicon.

Boron is prepared from boron trioxide by analogous methods. The trioxide, or one of its salts, preferably borax, is fused with mag-nesium or sodium; a flux is generally added to the mixture when the latter metal acts as the reducing agent; the double chloride of sodium and magnesium is used for this purpose in the technical extraction of boron. Another method of preparation consists in the electrolysis of fused borax; the sodium which is momentarily set free reacts with the excess of borax, liberating boron.

The alumino-thermic process gives good results only with silicon; a mixture of quartz, sulphur and aluminium is ignited by means of a fuse; the sulphur at once begins to combine with the aluminium, and the heat evolved by this reaction accelerates the reduction of the quartz

by the unchanged metal. The corresponding reaction with boron trioxide gives an aluminium boride which contains a very high percentage of boron, having the formula AlB_{12}. This compound was formerly mistaken for "crystalline boron." The metals employed in the reduction of silicon and boron compounds readily form intimate mixtures with both these elements, and sometimes combine chemically, giving silicides and borides. For instance, if silica is treated with the theoretical quantity of magnesium, the product of the reaction contains much magnesium silicide, the presence of which is indicated by the evolution of silanes on addition of hydrochloric acid. The so-called crystalline modifications of silicon and boron obtained when solutions of the elements in molten metals are cooled are generally contaminated with silicides and borides respectively, and often consist entirely of these derivatives.

Many molten metals, and also fused silicides and borides, can dissolve large quantities of silicon or boron, which crystallise out on cooling. These phenomena apparently involve the decomposition of silicides (or borides) stable at high temperatures into their constituent elements or into free silicon (boron) and a lower silicide (boride) of the metal as the temperature falls. Crystalline silicon separates very readily from these solutions, molten aluminium being the usual solvent. A saturated solution of silicon in molten iron deposits crystals of silicon on cooling, and these crystals are a normal constituent of pig-iron.

The halides of silicon and boron are more readily reduced by metals than the oxides. Potassium burns in silicon tetrachloride vapour, while sodium, magnesium, aluminium and even zinc react vigorously with the fluorides or chlorides of boron and silicon: $BF_3 + 3K \longrightarrow B + 3KF$. Double salts such as K_2SiF_6 or KBF_4, are more convenient than simple halides, which react only in the gaseous state. The interaction of double fluorides and metals takes place below a red heat.

Silicon can also be obtained from silicides. Thus when copper silicide is heated with sulphur the latter unites with the metal and a residue of silicon is produced.

The methods of preparation of titanium resemble so closely those of boron and silicon that a detailed description of them would be superfluous. Titanium dioxide can be reduced with carbon in the electric furnace. Another process consists in the electrolysis of calcium chloride in the presence of titanium oxide; the calcium which is first set free effects the liberation of the titanium. The metal is also prepared by reduction of titanium chloride or double chloride with sodium.

The preparation of these three elements resembles in many respects that of the strongly electropositive metals. The high heat of formation of the oxides renders their reduction with carbon difficult or impossible, and makes it necessary to use metals which have a very strong affinity

for oxygen. Silicon and boron behave as true non-metals in electrolytic reactions, for they are never liberated directly at the cathode, but only as the result of secondary reactions with the metals set free as immediate products of the electrolysis.

The methods of preparation of the various forms of *carbon* are described on pp. 137-145.

Isolation of the Rare Gases

Helium, Neon, Argon, Krypton, Xenon; Emanations.—The rare gases always occur in the uncombined state. The emanations result from radioactive transformations (see p. 82 and table facing p. 72), and the atmosphere is the most important source of the others, although helium is also obtained from other sources.

The percentage quantities of the rare gases present in the air are as follows :

	By Volume.	By Weight.
A . . .	0·932	1·285
Ne . . .	0·0015	0·001
He . . .	0·0005	0·00007
Kr . . .	0·0001	0·00028
Xe . . .	0·00001	0·00004

The simplest method of obtaining crude argon from the air is by fractional distillation. As the boiling point of argon lies between those of nitrogen and oxygen, the bulk of the nitrogen can be removed by allowing it to evaporate from liquid air, and then the remaining oxygen, which contains the bulk of the argon and a little nitrogen, can be carefully fractionated. In this way a gas containing about equal volumes of argon and nitrogen is obtained, and the nitrogen is then removed by one of the following methods: (*a*) The mixture is artificially mixed with an excess of oxygen, sparked, and the nitrogen oxides absorbed with caustic soda; the surplus oxygen is then removed by passing the gas over phosphorus or red-hot copper, or by explosion with hydrogen; (*b*) the carbon dioxide in the air is first removed by caustic soda, then the oxygen is absorbed with red-hot copper, and finally the nitrogen is converted into magnesium nitride by passing the gas over a mixture of lime and metallic magnesium. The second method is preferable.

Metallic calcium can also be employed as the absorbing agent, and has the advantage of uniting with all the three gases, oxygen, nitrogen and hydrogen, to form oxide, nitride and hydride respectively. If calcium carbide is used instead of the metal, the nitrogen is converted into cyanide or cyanamide. Lithium can also be used to remove nitrogen as Li_3N.

Three methods are available for the isolation of the rare gases

contained in crude argon. The gases may be separated from one another by diffusion, but this is a very troublesome process. Fractional distillation of the liquefied argon gives better results; the gases, of course, escape from the mixture in the order of their volatility: He $\longrightarrow$ Ne $\longrightarrow$ A $\longrightarrow$ Kr $\longrightarrow$ Xe (for boiling points see p. 41). This process is specially suitable for the separation of xenon, krypton and argon. The third method depends upon the principle that gases which are the most easily liquefied are the most readily adsorbed by porous bodies. Thus if the mixture of inert gases is treated with coconut charcoal at a low temperature, the three heaviest elements are adsorbed, while the gaseous residue consists of a mixture of neon and helium (Dewar). The neon can then be adsorbed by a fresh quantity of charcoal cooled in liquid air, and the helium left behind. A more complete separation of these two gases is effected, however, by surrounding the mixture with liquid hydrogen; at this temperature the neon solidifies, while the helium remains in the gaseous state and is easily removed.

Helium is a disintegration product of many radioactive bodies (see Chap. III). Thus helium is found in all minerals containing uranium and thorium; e.g. clevite, monazite, pitchblende, samarskite. The gas does not escape spontaneously, and is possibly retained in a state of solid solution. The helium is liberated when the mineral is decomposed by solution in acids or by treatment with suitable reagents in the dry way; e.g. alkali carbonates, bisulphates. The action of heat alone *in vacuo* also expels the gas; the quantity which escapes is inappreciable at temperatures below 300°, becomes considerable at 400°, and above 1000° the whole of the gas is expelled. Malakon contains helium but is free from uranium and thorium; it also gives off quantities of argon, though it is almost the only mineral which contains this gas. The largest quantity of occluded helium has been found in a specimen of thorianite, from which more than 10 c.c. of gas were evolved per g. of mineral. Helium is also present in considerable quantity in the dissolved gas of various spring-waters. For example, the mineral waters of Bourbon-Lancy contain 1·84 per cent. of helium (the total percentage of rare gas = 3·04); 547,500 litres of gas are evolved from these springs in a year, which is equivalent to a yearly production of 10,074 litres of helium (16,644 litres of rare gases). The natural gas of North America is at present the most prolific source of helium; it consists mostly of methane and nitrogen and never contains more than 2 per cent. of helium.

Helium is a disintegration product of many radioactive elements; e.g. 1 g. radium produces 0·158 c.c. of helium in one year. Since the speed of formation of radium from uranium is known, the age of a radioactive mineral can be estimated from a consideration of the relative quantities of uranium and helium which are present.[1]

[1] Strutt, *Proc. Roy. Soc*, 1908, 81, 272.

Actually helium nuclei are present in the more complex nuclei of atoms of many if not of all other elements (except H). Many elements with atomic weights which are exact multiples of 4, *e.g.*

C	O	S	Ca	Ti	Mn
12	16	32	40	48	56	etc.,

appear to consist only of a number of He nuclei, as no hydrogen is obtained when they are bombarded by α-rays from radium-C (*cf.* p. 10).

The emanations of the radioactive elements also belong to the group of inert gases; the best known of these members is radium emanation, also termed radon (niton). They occupy positions in the periodic system below xenon (for preparation see pp. 72, 82).

PREPARATION OF ELEMENTS—METALS

Alkali and alkaline earth metals—Aluminium and the rare earth metals—
Metallurgy of other base metals—Noble metals

The Alkali and Alkaline Earth Metals; Aluminium, etc.

THESE elements occupy to some extent a unique position among the metals; the methods of preparing them are similar in principle, but differ in degree from those used for other metallic elements. They are the most electropositive of all the elements, and consequently stand at the head of the electrometric series (*cf.* p. 151). The oxides and halides formed by metals of these groups are the most stable known, and in consequence they are difficult to prepare in the free state.

These elements can be obtained by the *decomposition* of three classes of derivatives: the hydrides, the azides and the amalgams.

The hydride method is utilised for the production of extremely pure barium, but otherwise has no practical importance. Actually, the hydrides are themselves mostly obtained from the metals. Magnesium and aluminium form no hydrogen compounds.

The azides, which are often explosive, are only suitable for preparations on a small scale; this method, however, gives the metals in the highest state of purity, since there is no possibility of contamination with by-products. (See p. 663 for the decomposition temperatures of azides.)

The amalgam method of preparation is applied more especially to alkaline earth metals. These metallic amalgams, which are produced by treatment of very strong solutions of the chlorides with sodium amalgam, are first concentrated by heating *in vacuo*, and then the excess of mercury is carefully distilled off. The metal still retains small traces of mercury, which cannot be expelled, and also some iron derived from the apparatus. A better method, which avoids the presence of these impurities, consists in the conversion of the amalgam into the hydride by the action of hydrogen, when the mercury simultaneously volatilises, and the metallic hydride subsequently decomposes at a higher temperature. Amalgams obtained electrolytically were formerly utilised for the preparation of the remaining metals of this group. At the present time they are produced only as a starting

material for the preparation of other compounds, *e.g.* the alkali hydroxides.

The metals of these groups can be isolated by displacement methods, both electrolytically from their ions and by purely chemical processes from compounds, among which the oxides, hydroxides and halogen derivatives are almost exclusively employed. Occasionally the sulphides are utilised for the same purpose. The reduction of the oxides, represented by the general equation: $MO + R \longrightarrow RO + M$, is only effected with facility by strongly electropositive metals, *i.e.* those which belong to the same group.

The Use of other Metals as Reducing Agents.—The separation of the alkali and alkaline earth metals by the action of magnesium or rare earth metals in the form of "Mischmetall" is attended with great violence. The heats of formation of the rare earth and magnesium oxides are greater than those of all other oxides (p. 441). When lithium carbonate is heated with magnesium powder the reaction is accompanied by a loud explosion; the corresponding reactions between magnesium and other alkali carbonates, although also proceeding to completion, become less vigorous with increase in the atomic weight of the alkali metal. The quantity of heat evolved during these reductions is sufficient both to reduce the alkali carbonate and to drive off the carbon dioxide. This method is particularly suitable for the preparation of rubidium and caesium.[1] These metals are also produced in radio valves by reduction of the chlorides with powdered Zr or Ti. Besides magnesium itself, other metals of this group set free the alkali and alkaline earth metals, provided a secondary reaction which results in the liberation of a large quantity of free energy is carried out simultaneously. A method based on this principle has been devised for the extraction of beryllium from its oxide; potassium chlorate is added to the aluminium employed as the reducing agent; a portion of the latter reacts with the chlorate with the evolution of a large quantity of heat which accelerates the main reaction between the aluminium and the beryllium oxide. The rare earth metals are only isolated with considerable difficulty by the alumino-thermic (Goldschmidt) process (*cf.* p. 199).

The hydroxides are generally used as the source of the alkali metals, while the alkaline earth metals are preferably extracted from their chlorides. It is an advantage to choose compounds which are easily melted; if necessary, the fusion temperature may be lowered by the addition of a flux. Thus sodium fluoride is easily reduced to the metal by aluminium in the presence of fluorspar. Magnesium chloride to which alkali chlorides have been added is reduced to metallic magnesium by sodium or potassium. Metallic calcium has also been much used as a reducing agent, since the calcium chloride which results is easily fusible. The addition of a flux is essential in the

[1] Graefe and Eckhardt, *Z. anorg. Chem.*, 1900, **22**, 158.

isolation of the non-alkaline earth-forming metals; otherwise, owing to their high melting points, the melts would have to be heated very strongly in order to obtain the metal in the reguline condition. The simple halides of these earth-forming metals are rather unsuitable as a source of the metallic components, owing to their volatility; double halogen compounds, such as Na_3AlCl_6, or Na_3AlF_6 (cryolite), or a mixture of these with sodium chloride, being less volatile, are preferably employed.

The reduction can be carried out in one of three ways: (a) the reactants are fused together in a crucible; (b) pieces of the reducing metal are introduced into the molten salts; (c) the halogen derivative, if readily volatile (e.g. $AlCl_3$), may be vaporised and passed over molten sodium. The most suitable conditions and the best metals to employ as reducing agents can, however, only be determined empirically, since difficulties in the reduction arise in practice which cannot be foreseen theoretically. For example, barium oxide is only partially reduced to metal by magnesium, as a suboxide of barium, Ba_2O, is produced which forms with the excess of magnesium an equilibrium mixture, the exact composition of which varies with the temperature: $Ba_2O + Mg \rightleftharpoons MgO + 2Ba$; consequently on distillation a mixture of both metals is produced. Again, the treatment of barium oxide with aluminium results in the formation, not of pure barium, but of an alloy from which the barium may with some difficulty be distilled off at a higher temperature. On the other hand, pure barium is obtained by the action of calcium on an excess of BaO. The reduction of the halides by metals is also impeded in some instances by unfavourable equilibria. Thus the equilibrium mixtures obtained by the reaction between strontium chloride and sodium: $SrCl_2 + 2Na \rightleftharpoons 2NaCl + Sr$, under all possible experimental conditions consist mainly of the original reactants. Nevertheless, all the metals of this group, including those of the rare earths except holmium, can be isolated by such methods.[1]

Reduction with metallic sodium was for a long time the principal process for the extraction of aluminium from its compounds. It is necessary that the sodium should be liberated as an intermediate product, and this may be done by heating wood shavings or carbohydrates with sodium aluminate. Technically, this method met with little success, and it was found that sodium could be replaced by other less positive metals, which could also be produced during the reaction; the aluminium formed an alloy with the excess of the other metals. The most interesting example of this method was the fusion of kaolin (aluminium silicate) with calamine (zinc carbonate) and coal, common salt being added as a flux. An alloy of aluminium and zinc was formed, and pure aluminium could be obtained from this, owing to the greater volatility of zinc at high temperatures. This process does not appear

[1] Klemm and Bommer, Z, anorg. Chem., 1937, 231, 138.

to have been worked out on any large scale. Iron, which is even less electropositive than zinc, can also displace aluminium, in particular from the sulphide. This method, which has also been suggested for the extraction of magnesium, consists in heating alumina in carbon disulphide vapour, or in hydrogen sulphide, and then treating the resulting aluminium sulphide with iron. Gay-Lussac and Thénard similarly obtained potassium by distilling the hydroxide with iron filings.

Reduction with Carbon.—The affinity of carbon for oxygen is less than that of the alkali, alkaline earth and other earth metals. It is therefore only possible to obtain the free metals by heating the oxides with carbon, provided sufficient energy is supplied; but the alkaline earth and other earth metals cannot thus be obtained, chiefly because they form carbides with the excess of carbon.

An intimate mixture of carbon and the alkali carbonates, produced by the carbonisation of the tartrates, was used in the oldest process for the preparation of the alkali metals. This mixture was heated in iron tubes, when the liberated metal distilled off. This method is not to be recommended for potassium, as the highly explosive carbonyl, $C_6O_6K_6$, is also liable to be formed. In a more modern method the molten hydroxide is run on to red-hot carbon (Netto). The alkali metal and carbon dioxide are formed; the former distils off, and the latter is absorbed by the excess of hydroxide, forming the carbonate, which flows away. The temperature used in this process is insufficient for the reduction of magnesium oxide; but if the magnesia is mixed with carbon, made into rods, and an electric arc struck between them, magnesium distils off.

In place of pure carbon, carbides or mixtures of carbon with other metals can be used. Calcium carbide especially has been employed for this purpose, as well as a so-called carbide, which is a mixture of iron and carbonised substances such as is obtained by the carbonisation of potassium ferrocyanide (Castner), and a crude mixture of iron filings and tar has also been used.

Electrolytic Processes. — Chemical methods for the preparation of these metals have now receded into the background in favour of electrolytic processes. The great tendency of the metals at the top of the electromotive series (p. 151) to form ions makes it difficult, or even impossible, to effect their separation from aqueous solutions. Metals above hydrogen in the electromotive series can be separated from aqueous solutions of their salts if mixed with other substances to make them less electropositive. Even the alkali metals can conveniently be obtained as amalgams by the use of mercury cathodes. These amalgams generate hydrogen very slowly, on account of their reduced electropositive character and because a considerable over-voltage is required for the discharge of hydrogen from mercury electrodes; the

E.M.F. of a hydrogen electrode, with mercury as a hydrogen carrier, is smaller than that of a hydrogen electrode with spongy platinum as the hydrogen carrier. The E.M.F. given in the usual electromotive series is derived from the tendency to form ions under suitable conditions, but this tendency may be completely different with other forms of the metals, or when they are mixed with other substances or previously chemically treated (*i.e.* by rendering "passive"). When, therefore, it is desired to separate by electrolysis a metal above hydrogen in the electromotive series, a change of this kind must be made to take place by the simultaneous precipitation of other metals to form a less electropositive alloy (magnesium is conveniently separated with nickel).

The hydrogen produced sometimes imparts a less electropositive character to the metal. Sodium can be obtained by the use of lead or zinc electrodes, as well as with mercury electrodes, while even "ammonium" can be isolated, in the form of an alloy, by the electrolysis of its salts with mercury electrodes. The effect of hydrogen in making metals less electropositive, as shown by over-voltage, extends at least as far as zinc in the electromotive series; zinc can even be separated electrolytically from acid solutions under suitable conditions.

Metals which lie above hydrogen in the electromotive series may be separated if all the hydrogen ions in the neighbourhood of the electrode have already been discharged by use of a high current density. The hydrogen is then no longer available for secondary reactions, and in consequence the metal is insoluble when once deposited by the current. Deposition is favoured by addition of colloids, which may tend to hinder diffusion of hydrogen ions to the electrodes, and by high concentration of the salt in solution, which provides a large excess of metal ions at the electrode. Any procedure which opposes the lowering of the hydrogen ion concentration at the cathode, such as agitation of the liquid, addition of strong acids, etc., is unfavourable to the deposition of the metal. Thus magnesium can be separated electrolytically from aqueous solutions of its salts by working with very concentrated solutions. Aluminium can be obtained by the decomposition of solutions containing potassium cyanide or organic compounds.

Even the more electropositive metals can be obtained from aqueous solutions by electrolysis if substances are added which reduce the dissociation, *i.e.* diminish the electrolytic solution pressure. Thus metallic calcium can be obtained from aqueous solutions of its chloride if methyl alcohol is added, and lithium from solutions of its salts in acetone or pyridine. Of course the waste of current is considerable, since much hydrogen is evolved, and these methods have no technical prospects. The difficulty is to select a solvent which undergoes no side reactions under the influence of the current.

Such a solvent may be obtained by melting the salt to be electro-

lysed, when part of the salt dissociates and dissolves in the undissociated fraction. It is advantageous to add other salts or compounds which are not electrolysed but serve as diluents. The conductivity is thus increased, the temperature of fusion is lowered, volatilisation of the substance to be electrolysed is prevented, and, in general, the conditions are more suitable for electrolysis. Sometimes the process goes on by separation of a substance from the solvent in the first place, whereupon the liberated material reacts with the dissolved substance to give the product required.

In the manufacture of the alkali and alkaline earth metals, the molten hydroxides or oxides are sometimes electrolysed, but the halogen compounds are more often employed. The method of electrolysis is conditioned by the disturbing factors that appear. One of the chief difficulties in processes employing molten electrolytes is that the metallic particles do not coagulate on separation, but disperse through the molten mass as a metal fog (see p. 105). On account of this, not only does the removal of the metal from the melt become impossible, but the fog also penetrates to the anode, with the result that the metal again combines with the non-metallic part which has been discharged there. Reactions also often occur between the liberated metals and the original salts. For example, the subchlorides $BaCl$ and $SrCl$ respectively are formed during the electrolysis of the chlorides of barium and strontium, and a similar phenomenon occurs in the electrolysis of sodium chloride.

The first of these difficulties is overcome if the density of the melt is different from that of the resulting metal, so that the latter readily rises to the surface and can then be skimmed off. It is sometimes advantageous to carry out the electrolysis at as low a temperature as possible, not only to economise energy but because the tendency of the deposited metal to form a dust or fog is less at lower temperatures. On account of this tendency, pure salts are not usually electrolysed, but mixtures of different halogen salts of the same metal are used ($KCl + KF$ for the preparation of potassium; $CaCl_2 + CaF_2$ or CaI_2 for the preparation of calcium). Alternatively, the halogen salt which is to be electrolysed is mixed with a salt of a more electropositive metal, which is either not separated by the current, or, if actually separated, at once displaces the original metal from its halide. Sodium chloride or lithium chloride is electrolysed for the preparation of sodium or lithium, with the addition of potassium chloride; and magnesium chloride is electrolysed in the form of its double compound with potassium chloride (carnallite). The preparation of barium and strontium by this method is unsuccessful, since it is not possible as yet to avoid the formation of the subchlorides.

Metals like aluminium, of which the oxides have very high melting points, can be obtained only at great cost by the electrolysis of the

molten oxide. On the other hand, the electrolysis of aluminium chloride is very difficult in practice, owing to its volatility; but it can be used in electrolytic processes with the addition of a flux, usually the alkali chlorides. The fact that the latter form double compounds with aluminium chloride does not affect the process, as these double compounds are extensively decomposed at the temperature of the melt.

Molten Na_3AlCl_6 and, more particularly, cryolite, Na_3AlF_6, mixed with other salts, are used in electrolytic processes. If, however, cryolite is employed, the fluorine evolved reacts with the carbon of the anode and escapes as carbon tetrafluoride. To diminish the loss of fluorine, chlorides (either Na_3AlCl_6 or NaCl) are added to the melt. The fluorine then displaces chlorine from these chlorides, and is kept back in the process. If the current density is sufficiently great the alkali metals may separate instead of aluminium, although they are more electropositive than the latter, but this does not affect the process, as they then react with the aluminium salt and liberate free aluminium. During the electrolysis of molten electrolytes, the initial separation of a more electropositive metal is of no disadvantage as regards current consumption, if it forms a relatively inactive alloy with the less positive metal required.

In the same way a strongly negative element initially deposited on the anode may then liberate a less negative element by chemical action. The more negative element thus remains in the system. The escape of chlorine can be diminished by the addition of oxides to the melt, so that the chlorine combines with the metal of the oxide, liberating oxygen. Aluminium oxide itself is difficult to electrolyse on account of its high melting point, but solutions in halogen compounds are used in electrolytic processes for the preparation of aluminium (Hall-Héroult process). This process possesses the great advantage that the heat generated by the passage of the current at a moderate E.M.F. is sufficient to keep the electrolyte fused. Therefore, in Grätzel's process, aluminium oxide is dissolved in the molten oxide and chloride of calcium. Some of the chlorine produced forms aluminium chloride, and the calcium liberated in turn displaces aluminium from this. In practice, however, mixtures of cryolite, common salt and alumina are usually electrolysed, the alumina being replaced as fast as it is used up. An artificial or purified cryolite is often used, which unlike the natural product is practically free from iron and silica, so that these impurities do not occur in the resulting aluminium.

Double sulphides of aluminium and the alkali metals have been electrolysed with success on the technical scale, instead of the halogen compounds. The theory of this method is similar to that discussed above.

The methods of preparing the rare earth metals closely resemble

those used for aluminium. When they are not obtained by the action of sodium on their chlorides (p. 188), electrolysis of the molten chlorides is adopted, but alkali chlorides must also be added to assist fusion. The electrolytic preparation of beryllium is carried out by the Grätzel process, a mixture of $2BeO$, BeF_2 and BaF_2 or NaF being used. It can also be made by the electrolysis of $KBeF_3$, or a mixture of $BeCl_2$ and NaCl. Electrolysis of $BeCl_2$ in liquid ammonia gives a very pure metal.

Preparation of the Metals from Manganese to Mercury in the Electromotive Series

MN, CR, ZN, FE, NI, CO, CD, SN, PB, CU, HG (AS, SB, BI)

The extraction of these elements from their compounds presents no great difficulties, as may be anticipated from their middle position in the electromotive series and in the table of heat of formation of oxides, etc. (p. 441). In practice their preparation is more difficult than that of the noble metals, but less energy need be supplied than for the liberation of alkali metals. The nearer these metals approach to the "noble" metals the lower the temperature required for their preparation from exothermic oxides, sulphides, etc., and the greater the number of possible reducing agents. Mercury, which behaves to a great extent like a "noble" metal, is liberated from its compounds by slight heating, and is precipitated from aqueous solutions of its salts by moderate reducing agents, while manganese, at the other end of the series, differs little from the metals of the preceding class in difficulty of preparation. Mercury is the only metal of this group obtained simply by heating the oxide to a moderate temperature. This method of preparation is possible for the other metals, but the required temperature is higher, as the heat of formation of the oxide is greater (*cf.* table on p. 441). For example, the formation of metallic copper from cuprous oxide takes place above 2000°, while the preparation of the other metals is still more difficult, and the decomposition temperature of many of their oxides has not been ascertained.

Reduction with Hydrogen.—The ease with which the oxides or other compounds are reduced to the metals by hydrogen falls off in a similar manner. Manganous oxide can only be reduced to manganese at 2500°, while the other oxides are reduced more easily the less their affinity for oxygen (see tables on pp. 441, 445). The reaction · $MO + H_2 \rightleftharpoons M + H_2O$, proceeds to an equilibrium, which lies more on the side of the formation of the pure metal, the more the heat of formation of water exceeds that of the oxide of the metal. It must, however, proceed up to a certain concentration of metal, when the heat

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of formation of water is very much less than that of the metal oxide. If a current of hydrogen is used, so that the water formed is continuously removed, more water is produced from the oxide in an attempt to maintain the equilibrium. The steam is carried away by the stream of gas so that the oxide is finally completely reduced. This reduction can be carried out for all metals from manganese downwards, but not for those in which the heat of formation of the oxide is equal to or greater than that of manganese. The boundary is fairly sharp, and the concentration of water vapour must clearly exceed a certain minimum value, in order that the water vapour may be carried off; in the equilibrium of manganese oxide, and of all other elements above manganese, this value is not attained.

Certain oxides which can be reduced by hydrogen offer a definite resistance to reduction. Cupric oxide is not reduced by hydrogen at room temperature, although mere application of the equilibrium equation to this reduction indicates that it should be possible (the reduction of silver oxide is practicable at room temperature), but in practice considerably higher temperatures are necessary. The temperature at which reduction is first observed can be reduced considerably. There is, however, a minimum temperature below which no reduction occurs. At low temperatures the concentration of water in the reduction zone may not correspond to the value obtained by experimental measurements, on account of adsorption of water vapour on the oxide or because of other factors.

Since reduction with hydrogen can be undertaken at relatively low temperatures, it serves for the preparation of metals in a finely divided state. Pyrophoric metals (*e.g.* iron) are prepared in this way, as well as those used as contact catalysts, on account of the great surface developed (nickel, by reduction with hydrogen). Sometimes the oxalate is reduced instead of the oxide (cobalt). The oxide formed in this way is already in a very fine state of division.

At higher temperatures ammonia can be used with advantage as reducing agent instead of hydrogen. At 200° this gas is extensively dissociated into hydrogen and nitrogen, and an equilibrium is set up. Thus the hydrogen is employed in its nascent (atomic) form. This method is not applicable to metals which readily form nitrides with nitrogen. Ammonia itself need not necessarily be employed, but solid ammonium chloride can be used instead. At the dissociation temperature of this salt (330°), extensive decomposition of ammonia takes place, with the formation of hydrogen.

Technically, these reducing agents scarcely come into consideration. As in the electro-chemical methods, only the oxides, the sulphides, and sometimes the chlorides, are used as the initial substances in metallurgical processes. If the ore does not already consist of one of these classes of compounds, it is first converted into one of them.

Carbon or iron are used almost exclusively as reducing agents for the metals discussed in this section.

Preparation of the Ore.—The direct working-up of the crude ore with the reducing agent is only possible with very pure materials. The removal of as much as possible of the gangue is important, and inasmuch as this cannot be done mechanically with finely divided materials, *flotation* processes are now commonly used. These methods depend on differences in the contact angles of various constituents with water; the surface tension of the water, and hence the efficiency of separation, is altered by the addition of frothing agents. The powdered mixture is stirred up with water and an oily liquid, such as petroleum, which wets the ore but not the gangue. The latter consequently sinks. The addition of foam-producing materials assists the flotation of the ore; the process works particularly well with sulphide ores. The gangue is further removed by the formation of *slags* in the reduction process itself. The substances added may be of a basic nature (lime, ferric oxide), or acidic (silicic acid, acid silicates, or, in more delicate operations, acid borates, borax), these fluxes being so constituted that they form salts with the impurities; thus it must be acid to remove basic impurities, and basic for acid impurities. The resulting salts (slags) should fulfil certain conditions. The slag should give a thin liquid melt, so that it can easily be drawn off mechanically from the metal, and also in order that it may protect the metal from the action of air. Secondly, its melting point should be low, since many metals have a relatively low boiling point, and the metal would otherwise be vaporised before the slag had fused. It should contain no chemical constituent capable of reacting with the metal, and slag formation should result only after reduction to the metal has taken place, or the metal oxide would readily enter into the slag as the silicate, and considerable waste would result.

It is the task of the metallurgist to select a suitable composition for the slag. For instance, the calcium silicate formed from an ore containing lime must possess a suitable degree of acidity. Normal silicates and trisilicates melt with difficulty, while the melting points of disilicates are usually lower. The silicates of calcium, magnesium and aluminium are melted only with great difficulty, and if their formation cannot be avoided, their melting points are lowered by the addition of alkali (glass is used in the melt). The silicates of the heavy metals, particularly of manganese, are easily melted, and for this reason a small quantity of iron in the slag is an actual advantage. Other substances can also be added to the melt as fluxes (*e.g.* fluorspar).

A further operation, which sometimes takes place simultaneously with the melting of the slag, or, at any rate, in the same process, is the conversion of the ore into the oxide, sulphide, or a mixture of these two, or into water-soluble compounds such as the chloride. The

conversion of many carbonates into oxides is brought about by simple heating, *e.g.* with zinc carbonate (roasting), while with many sulphides it can be accomplished by heating with free access of air (calcination). Oxides or hydroxides occur only rarely in nature, but they do not require treatment before reduction. Tin usually occurs as tin dioxide (tin stone), and iron also occurs as oxides or hydroxides, which can be reduced without much previous preparation.

Reduction with Carbon.—Oxides of metals are frequently reduced with carbon. It is not possible that reduction proceeds simply according to the equation : $2MO + C \longrightarrow 2M + CO_2$, for considerable quantities of carbon monoxide appear regularly in the escaping gases. At the temperature prevailing, *e.g.* in the manufacture of iron, carbon dioxide is not stable, but exists in equilibrium according to numerous possible systems, which must be considered :

$$C + O_2 \rightleftharpoons CO_2 \qquad 2CO \rightleftharpoons C + CO_2 \qquad 2CO + O_2 \rightleftharpoons 2CO_2$$
$$Fe_3O_4 + CO \rightleftharpoons 3FeO + CO_2 \qquad FeO + CO \rightleftharpoons Fe + CO_2$$
$$3Fe + 2CO \rightleftharpoons Fe_3C + CO_2 \qquad 4CO_2 + Fe_3C \rightleftharpoons 3FeO + 5CO.$$
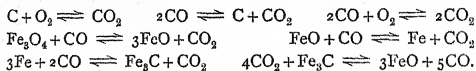
The carbon monoxide still contained in the emerging blast furnace gas cannot be utilised for the reduction of new iron oxide, since new carbon dioxide would result and, as soon as the concentration of this exceeded the equilibrium value, it would again oxidise some of the iron. Increasing the height of the blast furnaces, and prolongation of the time taken by the gases to pass through it, can, for the same reason, have no practical utility above a certain point.

On account of the great importance of the manufacture of iron in the blast furnace, the equilibrium has been studied in detail.[1] It was found that Fe_3O_4 is stable in the presence of carbon, carbon monoxide and carbon dioxide in the blast furnace, at temperatures below 647°, while FeO exists between 647° and 685°. Above 685° reduction to metallic iron takes place. Thus the following exist in equilibrium, in the presence of one another,

at 647° : C, CO, CO_2, FeO, Fe_3O_4,
at 685° : C, CO, CO_2, FeO, Fe.
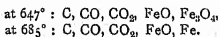
In the blast furnace the reduction of the different oxides of iron takes place at different temperatures. It is brought about almost exclusively by gaseous CO, which circulates through the ore, but reduction by means of solid carbon is not excluded, although it is more difficult on mechanical grounds. If the oxides of the metals are fusible (PbO, SnO_2), they can be reduced directly by carbon. Carbon monoxide reduces Fe_2O_3 at lower temperatures than Fe_3O_4, while this, in turn, is reduced at lower temperatures than FeO. Reduction of an oxide usually proceeds first to the next lower oxide, although direct reduction to the metal is also possible. If the temperature is fixed, reduction proceeds only until the concentration of the CO_2 formed attains a certain value. If this is exceeded, the higher oxide and CO are again formed from the lower oxide and CO_2. At lower temperatures the CO can exert no reducing action. Below 685° it is decomposed by the catalytic action of

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[1] *E.g.* B. Schenck and his collaborators (1903-4), Baur and Glässner, *Z. physikal. Chem.*, 1903, 43, 354.

metallic iron, CO_2 and finely divided carbon being produced ($2CO \rightleftharpoons C + CO_2$). The resulting absence of reducing action causes the formation of "scaffolds" in the blast furnace. If, however, the temperature is raised above 685°, the CO_2 and C again react, with the formation of CO, so that the "scaffolds" are removed.

Each oxide of iron in equilibrium with the oxides of carbon gives different concentrations of CO and CO_2 at a given temperature. Thus the equilibrium $FeO + CO \rightleftharpoons Fe + CO_2$ corresponds at 680° to a minimum value in CO_2, while, on the other hand, the equilibrium for Fe_3O_4 produces a maximum value of CO_2 at 490°. Unfortunately, the latter temperature is still about 200° removed from the temperature of the formation of free iron. The most efficient conditions, when the temperature for the formation of iron coincides with the maximum value of CO_2 in the gas mixture, unfortunately, do not occur, and the abundant unused CO escapes in the blast furnace gas and must be utilised in other ways, e.g. for driving gas engines or heating the blast. The equilibrium temperature differs according to the nature of the smelted iron which remains, and if it is to be rich in carbide, Fe_3C (cementite), the temperature is very considerably reduced. The nature of the ore also has an influence on the temperature of preparation and on the equilibrium. If the ore contains manganese, the displacement is particularly great, since manganese, like many metals more electropositive than iron, possesses a great affinity for oxygen, and consequently reduces more CO_2, so that the blast furnace gas will be richer in CO. (For the equilibria of the oxides of carbon see p. 782 et seq.)

Almost the entire production of iron and of tin is derived from oxide ores, which can be directly reduced to the metal by carbon. Natural zinc oxide and, under some conditions, cupric oxide are also reduced to the metal by carbon, but for the latter the addition of scorifying agents and fluxes is necessary. When a metallic oxide, as in zinc silicate (willemite), is combined with an acid radical which is not affected by the reduction, but which can be removed, either by a flux or by mechanical separation, it can be worked as a simple oxide.

Sulphide Ores.—The sulphide ores are only slightly reduced by carbon. Experiments on reduction in which carbon disulphide is formed at the same time as a by-product, thus: $2MS + C \longrightarrow 2M + CS_2$, have not been applied technically. The sulphide ores must first be converted into oxides. Only the "noble" metals, of which the oxides readily lose oxygen, can be obtained from the sulphide ores by smelting with lime, which is thereby converted into the sulphide and sulphate:

$$4HgS + 4CaO \longrightarrow 4Hg + 3CaS + CaSO_4.$$
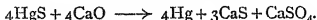
With the baser metals, the sulphur must be burned off by roasting (heating the dry ore with free access of air). It is often unnecessary, however, to convert these ores completely into oxides; they are often partially roasted and the oxide or sulphate produced allowed to react with the unchanged sulphide present. In this way sulphur dioxide and the metal are formed. This partial roasting is used for the extraction of copper:

$$CuS + 2CuO \longrightarrow 3Cu + SO_2,$$
or
$$Cu_2S + CuSO_4 \longrightarrow 3Cu + 2SO_2.$$
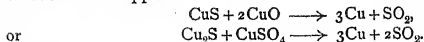
The metal can also be extracted by strongly oxidising to form the

sulphate, which is then reduced by carbon in the presence of lime, which may form calcium sulphate as an intermediate stage, but is finally reduced to the sulphide

$$CuSO_4 + CaO + 3C \longrightarrow Cu + CaS + 2CO_2 + CO.$$
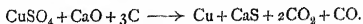
Natural copper sulphide and nickel sulphide cannot be worked directly without further treatment, as they contain great quantities of impurities, especially iron, arsenic and antimony. The desired metal must first be concentrated in the sulphide (fusion for matte). Arsenic can first be partly removed by roasting, on account of the volatility of its trioxide, after which most of the iron can be withdrawn as slag. Thus a melt is obtained free from arsenic and antimony and poor in iron, but still containing much sulphide. This is known as matte or "coarse metal." The products in the extraction of copper, and in similar processes, comprise "coarse metal" and slag, which consists chiefly of the silicates of calcium and iron, and the so-called speiss which consists of arsenides and antimonides, and always contains sulphur. There are also formed "iron sows," which are really speiss very rich in iron, and finally, in the colder parts of the furnace, the "tutty," which contains the oxide and sulphide of zinc. The speiss occurring in nature is, in part, very rich in nickel and cobalt, and is especially suitable for working for these metals. Also, if the speiss is roasted with sand and coke and the iron scorified, an enriched speiss is first produced. Sometimes it is not expedient to drive off the arsenic as its trioxide, but to convert it to arsenate. "Zaffre" is a cobalt arsenate obtained by roasting in this way, which is afterwards worked up for cobalt by wet processes.

Nickel-copper ores, after concentration and partial roasting, are smelted either in blast or reverberatory furnaces to give a matte of iron, nickel and copper sulphides, which acts also as a collector of the platinum metals (see p. 213). The matte is blown in a converter to remove iron, and the subsequent treatment of the resulting Bessemer matte of copper and nickel sulphides depends on whether nickel is to be produced by the carbonyl or the electrolytic process.

In the carbonyl process, the matte is ground and calcined to oxides :

$$(Cu, Ni)S + 2O_2 \longrightarrow CuO + NiO + SO_2.$$
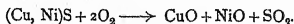
The copper oxide is then leached out by 12 per cent. sulphuric acid :

$$NiO + CuO + H_2SO_4 \longrightarrow NiO + CuSO_4 + H_2O.$$
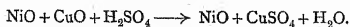
After drying, the nickel oxide is reduced by water-gas at $350°$:

$$NiO + H_2 + CO \longrightarrow Ni + H_2O + CO.$$
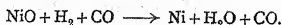
The reduced nickel is then purified as described on p. 201.

In the electrolytic process, copper and nickel sulphides are separated

by the Orford process. The Bessemer matte is mixed with coke and sodium bisulphate and smelted in blast furnaces. The charge separates into two layers, "tops" consisting of a double sulphide of sodium and copper, and "bottoms" consisting of nickel sulphide. In this process platinum metals go mainly with the nickel, whereas gold and silver follow copper. As the separation is not sharp, the process is repeated separately with the "tops" and "bottoms." The final "tops" are blown in converters, whereby sodium sulphide is oxidised to sodium sulphate and the copper sulphide is converted to blister copper, which is refined electrolytically. The "bottoms" (nickel sulphide) are crushed and then roasted to oxide, which is reduced to metal in reverberatory furnaces. The resulting nickel, containing about 2 per cent. of copper, iron and precious metals, is cast into anodes and refined by electrolysis. The anode slimes, which separate during electrolysis, contain the precious metals.

Reduction by Metals.—While carbon is the typical reducing agent for oxide ores, sulphides can be reduced by iron, which is converted into iron sulphide. For example, zinc sulphide cannot be directly reduced by carbon, but can be reduced by iron; mercury is obtained by distilling cinnabar with iron; antimony sulphide is also smelted with iron and a flux; bismuth ore is worked similarly. The latter contains cobalt and arsenic, besides bismuth and sulphur, and gives a melt consisting of three layers. The light cobalt speiss (cobalt arsenide) collects above the heavy fusible bismuth, while the slag containing iron forms the top layer.

Metals other than iron can also be used for reduction, especially those of a more pronounced electropositive character, such as aluminium (H. Goldschmidt). Since aluminium is considerably dearer than iron, it is employed only for the preparation of the basest metals of this series, especially for the extraction of manganese, chromium and vanadium.

Aluminium is used in the form of powder and is intimately mixed with the oxide to be reduced. The reaction is started by igniting in the mixture a pill containing magnesium powder and barium peroxide, from which projects a little piece of magnesium ribbon like the stalk of a cherry, to communicate the ignition ("ignition pellet"). The whole mass is contained in a Hessian crucible, or some other refractory vessel, imbedded in sand. The reaction soon sets in rapidly through the entire mixture, with explosive velocity in the oxides of the nobler metals (copper), but slower with baser metals, and with the development of so much heat that the metal becomes white hot and melts. Suitable mixtures of aluminium and iron oxide are sold as "thermit," and are used for the direct welding of iron objects as the iron is produced in a molten condition. For the reduction of the more refractory oxides, such as those of chromium and manganese, calcium borings are mixed with the aluminium, when the former metals are reduced as easily as iron. Since their reduction by carbon takes place only at very high temperatures, the aluminium process offers great advantages for the preparation of these expensive metals, especially as they are obtained free from carbon. Manganese oxide can also be reduced by

carbon when melted with a flux, such as glass, lime and fluorspar, in an electric furnace, but the metal absorbs carbon and is very rich in carbide.

Apart from the methods mentioned above, those used for metals adjacent to chromium and manganese in the electromotive series, and in heat of formation of oxides, can also be employed. Chromium is formed by the reduction of its oxide with calcium, magnesium, silicon, boron or calcium carbide. It is possible also to reduce nobler metals by these methods; for example, the reduction to zinc by silicon, aluminium or calcium carbide has already been known in the laboratory for a long time, and also the reduction to cobalt with " Mischmetall " (metals of the rare earths), but these processes have only been utilised technically in recent times.

Separation by Distillation and Liquation.—While most metals must be obtained by the reduction of their compounds, copper, bismuth and mercury are found in appreciable quantities in the free state in nature. Mercury is obtained by simple distillation, copper by electrolytic refining, as described below, while bismuth is melted out of its gangue (matrix) by simple heating in a tube furnace. Its low melting point (269°) makes it especially suitable for this method of liquation.

Some other metals, of low boiling points, can be isolated by distillation from the mixtures of metals which are obtained as by-products in the working-up of ores. Thus metallic zinc distils off during the smelting of lead ores or the heating of raw lead containing zinc; cadmium vapour forms the first fraction during the preparation of zinc. Arsenic can be sublimed by heating ores containing it.

In general, the mechanical separation of a reduced metal from its slag, or from other metals present as impurities, turns upon its physical properties, especially the melting point and boiling point. Metals of low boiling point, such as zinc and cadmium, can be distilled off as they are formed if the reduction temperature is high enough. The great quantities of gases which escape during the burning of the carbon are disadvantageous in these processes, since the consequent dilution of the zinc vapour hinders its condensation into liquid drops. Many small solid particles are formed ("zinc dust"), and, as these also contain considerable quantities of oxide, they must be remelted and again reduced for the production of compact metal. Sometimes the formation of dust is important, especially when oxide by-products are formed, owing to the considerable waste arising from the complete escape of the dust. This resembles ammonium chloride fog, and is similarly a solid-gas colloidal system which settles slowly. Experiments have indicated that, while dust chambers are useless, neutralisation of the electric charge which hinders settling out of the particles can be brought about by a high tension silent discharge. The amount of oxide contained in the zinc dust is lessened if the heat necessary for the

reduction of the ore by carbon is not provided by the combustion of carbon in air but is supplied electrically.

The formation of oxide can never be completely avoided, since the carbon dioxide formed during the reduction attacks the vapour of the metal. This action is more rapid and violent in the production of zinc than in that of iron, since zinc is exposed in the gaseous form, while the liquid iron offers a smaller surface for attack. The carbon dioxide in the gas leaving the blast furnace can be reduced to only 2·5 per cent. by working at about 600°, with the result that this action is greatly lessened; it is first troublesome when more than 5 per cent. of the gas mixture consists of carbon dioxide. Not only has electric heating stood the test in the preparation of zinc, but it has been used in other processes, e.g. for the production of copper and steel. The current serves only as a source of heat without exerting any electrolysing action. Involatile metals, such as iron, collect in the liquid state in the lower part of the furnace during the reduction, and are drawn off. Sometimes another metal is added to assist the liquefaction, particularly if it can readily be removed later on. The extraction of mixtures containing metals by means of mercury is especially useful, as amalgams are readily formed on heating, and the metal can be obtained by a kind of washing-out process. The metal is isolated from the amalgam by boiling off the mercury. This method is directly applied to the baser metals, particularly those difficult to fuse, such as manganese and chromium. Extraction by amalgam formation is now applied in most electrolytic processes.

Nickel is converted into nickel carbonyl, $Ni(CO)_4$, for the extraction of the metal. This compound, p. 791, has a low boiling point, and is formed when gaseous carbon monoxide passes over the reduced ore. It is carried off by the stream of gas at the working temperature of 50°, and later is brought into contact with fireclay shapes or nickel pellets heated to 180°-200°, when it is again split up into nickel and carbon monoxide. The gas is returned to the process and the nickel is deposited in a very pure form (Mond process).

Wet Processes.—Besides the processes for the extraction of metals carried out at high temperatures there are others in which solutions form the intermediate stages (" wet processes "). It is possible to treat many ores directly with solvents which react chemically with them. Thus copper is extracted from burnt pyrites by digestion with sulphuric, sulphurous or hydrochloric acids, with ammonia or with ferrous chloride solution; the latter gives, with the cupric oxide, a mass containing cuprous or cupric chlorides and ferric oxide. For the preparation of cupric chloride it can be leached with ferric chloride, and the resulting ferrous chloride regenerated. There are various other useful methods of preparation; for example, water-soluble copper sulphate is formed from burnt pyrites by weathering. In other processes the

dry ore is subjected to the action of chlorine, preferably in the warm. The chlorinated product is then either extracted with water (copper and nickel), or if readily volatilised is directly distilled off. Sizzle (waste tin plate) is thus detinned by extraction with chlorine gas, when liquid tin tetrachloride runs off; antimony ores are converted by dry chlorination into antimony trichloride, which is vaporised and collected in a solution of common salt; arsenic trichloride can be distilled off from arsenic ores by heating with ferrous chloride. The separation of lead and zinc, which is a difficult metallurgical process, can readily be brought about if the sulphide ores are subjected to the action of chlorine in the presence of hydrochloric acid. Both the zinc and the lead go into solution, and the lead present as H_2PbCl_6 is precipitated as $PbCl_2$, when the excess chlorine is removed by blowing in air or by reducing agents.

Conversion into water-soluble sulphosalts is used for the extraction of mercury, arsenic, antimony and tin, which are usually treated with alkali or alkaline earth sulphides. This was formerly used for the regeneration of tin from sizzle. Alternatively, the sizzle was allowed to stand in caustic potash in the air, when the tin was converted into the soluble stannate and thus washed away from the iron. The mercury sulphosalts are converted by precipitation with acid into the sulphide, which is then worked up by dry methods. The resulting solutions of other chlorides, sulphates or sulphosalts are acted on by metallic iron; this base metal precipitates the nobler metals ("cementation"). Thus copper, arsenic, antimony and bismuth are separated in the metallic form. The preliminary removal of impurities by chemical means is only undertaken when they are present in considerable quantity; e.g. in the extraction of cobalt from roasted zaffre (see p. 198), after dissolving in acid and adding ferric compounds, arsenic acid is removed by fractional addition of milk of lime. In nickel ores, again, a considerable separation of impurities can be effected by fractional solution of the roasted ore in acids. Similarly, cadmium containing zinc can be purified from the latter by fractional extraction with dilute hydrochloric acid, which dissolves the baser zinc more readily than the cadmium; if any cadmium is dissolved in the first place it is subsequently precipitated by the metallic zinc present.

The precipitation of metals from aqueous solution by reducing agents, though not much applied on a technical scale, is a phenomenon of general interest. Hydrogen can be used as the precipitant, but only for those metals which have less tendency to ionise than hydrogen itself. If, for example, the relatively base metal zinc is precipitated from a solution of one of its salts in a finely divided condition, it is at once redissolved by the acid set free, while copper remains unattacked by the acid under these conditions. When, however, salts of base

metals are treated with hydrogen under pressure, the metal is precipitated, but owing to the reaction being reversible it comes to a standstill when the acid formed is sufficiently concentrated to attack the metal. It is not, however, possible to account for the whole of the observed processes on theoretical grounds—even if pressure is applied a certain temperature must be reached before the action sets in.[1] It is found that mercury, copper, cobalt, nickel, lead and bismuth are liberated from their salts under these conditions, but not iron or zinc.

Compounds which give nascent hydrogen reduce metallic salts in the same way; thus stibine liberates the metal from bismuth or mercurous salts.

Yellow phosphorus has a reducing action on the salts of the nobler metals similar to that of a base metal. If a stick of phosphorus is placed in a solution of copper sulphate it becomes covered with a thick red coating of the metal. If the stick is then placed in hot water so that the phosphorus melts out, the copper sheath remains behind. When a piece of phosphorus is wrapped round with lead foil and then dipped into lead nitrate solution, metallic lead is deposited in crystals on the foil and phosphoric acid is produced in solution. The lower acids of phosphorus also precipitate metals from solution; hypophosphorous acid gives free bismuth, silver and mercury; copper sulphate gives the so-called cuprous hydride, whereas with cupric chloride, cuprous chloride is formed.

Hyposulphurous acid, $H_2S_2O_4$, behaves in this respect like hypophosphorous acid and tends to give colloidal solutions of the metal set free. The reaction may proceed yet further, the metal first formed being converted to sulphide. One of the most useful reagents for the preparation of colloidal solutions of the metals by reduction is hydrazine, especially when protective colloids are present; as the free base is less stable than the salts, the reduction proceeds most rapidly in alkaline solution. In the same way the reducing action of hydroxylamine is often more pronounced in alkaline liquids, and organic reducing agents like cane sugar are also more active under these conditions. It is possible that the ions present in the alkaline solutions are different from and more easily oxidised than those in acid solution. This is true at any rate for the compounds of tin; the stannous ions present in acid solutions of tin salts can be oxidised to $Sn^{····}$ ions, but much less readily than the SnO_2'' ions present in alkaline solution can be converted to SnO_3'' ions. This accounts for the different positions of acid and alkaline stannous chloride solutions in the oxidation and reduction series (p. 164). All the ordinary reducing agents give the free metal from salts of metals more electronegative than hydrogen, e.g. copper, bismuth, arsenic and mercury.

[1] Ipatiev, *Ber.*, 1909, 42, 2078.

Electro-chemical Processes.—The metals of this group are isolated by the electrolysis of aqueous solutions and not from fused compounds. Manganese, it is true, can be prepared by the electrolysis of the fused double chloride; and electrical heating is often applied in the ordinary reduction processes, *e.g.* for zinc and iron, but the process remains an ordinary chemical reaction and no discharge of ions takes place under these conditions.

Electrolysis is used as a method of obtaining or at least of purifying copper, and to a lesser degree nickel, tin, lead and bismuth. Only small quantities of iron are dealt with by this method. The electrolytic method is used only for preparing specially pure iron (p. 206); similarly, the application of this method to the winning of metallic zinc does not compete with the ordinary metallurgical processes, in spite of the high losses owing to the formation of zinc dust, etc., in the latter, unless very cheap current is available or ores which cannot be worked up in other ways are used. Zinc free from lead is obtained by electrolysis, but the application of this method is made more difficult by the deposition of the metal in a flocculent form, so that it tends to short-circuit with the anode.

Copper.—The great advantage of electrolytic methods of metal production lies in the possibility of combining purification with extraction. Undesirable impurities can be removed and valuable ones collected (*e.g.* silver and gold). The purification of raw copper is a good example of the application of the method. It is essential that the copper should be of a fairly high degree of purity to begin with; attempts to obtain pure copper direct from copper ores, by making these the anode, have not been attended with much success. The ores are bad conductors and do not form satisfactory anodes, as they rapidly disintegrate. When, however, copper of 98-99 per cent. purity is used as anode, the metal deposited on the cathode contains as little as 0.05 per cent. of impurities, and the noble metals present, which are not removed by other metallurgical methods, can be obtained as by-products.

The process consists in using the raw copper as anodes in an approximately normal solution of copper sulphate and sulphuric acid. The pure metal is deposited from the liquid on cathodes of thin sheet copper, while both copper and other base metals present such as iron, nickel, cobalt and zinc, go into solution from the impure anodes. If the current density is carefully regulated, only the copper is deposited, while the other more electropositive metals remain in solution. The crude copper also contains metals which are less electropositive than copper; these require a higher E.M.F. to effect solution, and if this is regulated so that only copper is dissolved they remain behind at the anode. The gradual removal of the copper which keeps these impurities together results in their being deposited beneath the anodes as the anode mud.

This mud contains cuprous sulphide, selenium, tellurium, silver, gold, palladium and a little platinum. The quantities of silver and gold are too small to be removed by any of the usual processes, but in the bulk the quantities are considerable.

Although it is fairly easy to prevent either the solution or the deposition of metals which differ somewhat largely from copper in their electro-chemical properties, there are some which approximate to it in these respects, and in consequence tend to follow it from anode to cathode. Among these are antimony, arsenic and bismuth. The presence of these metals is undesirable in the purified copper—they change the red colour of the pure copper to a greyish tone, and even a few thousandths of a per cent. has a marked effect in diminishing the conductivity of the metal. The tendency for these substances to be deposited is greater when the concentration of their ions becomes high; the concentration of copper ions at the cathode then becomes low, and the impurities are deposited in place of the desired metal. This local concentration of these ions can be avoided by stirring the liquid (e.g. by an air blast), or by running off the liquid near the cathode when it becomes weak in copper. The frequent changing of the electrolyte to avoid high concentrations of arsenic, antimony and bismuth is very inconvenient, as it is necessary to evaporate the liquid to recover the copper sulphate.

The time factor is important in this process, as the longer it takes to purify a given quantity of copper the greater the overhead charges are in proportion; as the rate of deposition depends on the current density, it is necessary to keep this as high as is compatible with the avoidance of practical difficulties. If the current is too large the cathodes become rough and the deposit of copper may even become slimy. As the deposit is greatest on the parts of the cathode nearest the anode, there is a tendency for irregularities in the deposit to become more pronounced and to short-circuit with the anode.

Among other difficulties the most important is the formation of cuprous sulphate, Cu_2SO_4, during the electrolysis. When this takes place the concentration of free acid in the solution becomes altered. It can be restored to the original value if the liquid is electrolysed with anodes which are not attacked (e.g. lead), when the excess of copper is deposited and no new copper goes into solution.

Lead.—The electrolytic purification of lead is undertaken with the same objects as that of copper — the elimination and recovery of impurities which cannot be dealt with by the ordinary metallurgical processes. The more important of these are silver and bismuth; it is particularly necessary to eliminate the latter, as lead which contains bismuth does not give a pure white lead. The raw lead (work lead) is electrolysed in a solution of hydrofluosilicic acid, since sulphuric and hydrochloric acids give sparingly soluble lead salts. Further, the

lead is deposited from this solution in a smooth deposit and not as
needles, which it usually tends to form. Both bismuth and silver
fall into the anode slime, and the bismuth is recovered from this
impure product by electrolysis in strong hydrochloric acid solution.

Nickel.—The isolation of nickel by electrolysis is usually adopted
when the nickel is in solution at one stage in the working-up of the
ores. The purification of nickel by the method adopted for copper is
not practicable, as the nickel anodes disintegrate too rapidly. It is
therefore necessary to dissolve the nickel previous to the electrolysis
and to use insoluble anodes, *e.g.* of lead dioxide. As the nickel is
deposited on the cathode, a corresponding quantity of free acid appears
in solution, which must be neutralised by the addition of precipitated
nickel hydroxide. The refining of nickel containing copper—an im-
portant process—can be undertaken by making use of the precipitation
of the more electronegative copper from the electrolyte, so that the
latter becomes richer in nickel. Thus anodes of cupro-nickel or of
matte containing these two metals can be electrolysed in a copper
sulphate solution ; as copper is deposited on the cathode, both copper
and nickel go into solution at the anode and thus the solution becomes
richer in nickel. The residual copper in the solution is then precipi-
tated by a chemical method and the pure solution of nickel electrolysed
with a lead dioxide anode to deposit the nickel. Difficulties arise
in this process only when iron is also present—the deposit of nickel on
the cathode has then a marked tendency to peel off.

Chromium.—The deposition of chromium takes place on the cathode
from a hot solution of CrO_3 (20-30 per cent.) containing sulphuric acid
(0·1-0·3 per cent.).

Iron.—All the difficulties mentioned before are accentuated in the
deposition of iron by electrolysis. They can be avoided in some
measure by keeping the current density low and the temperature high.
Under these conditions the iron contains less hydrogen than when
liberated at a lower temperature or with higher current density, and
the tendency of the deposit to peel off is connected with the simultaneous
liberation of hydrogen. The baseness of the metal is the cause of this
co-liberation of hydrogen ; in fact, it is only on account of polarisation
and passivity effects that the iron can be deposited on the cathode at
all, for its tendency to form ions is not much greater than that of
hydrogen itself. The hydrogen which the iron contains makes the
subsequent treatment of the iron difficult ; it is very soft and is only
suitable for purposes for which a very malleable iron can be used.
The hydrogen can be removed by heating the iron after removal from
the bath, and as it also contains some carbon and oxides of iron,
hydrogen and carbon monoxide are liberated when the iron is ignited
and the injurious impurities thus removed.

In order to avoid the formation of large quantities of hydroxide

during the electrolysis, the liquid is kept weakly acid by the addition of boric acid. The addition of ammonium salts also serves to repress the concentration of hydroxyl ions below the concentration required for the precipitation of the ferrous hydroxide.

When a high temperature is used in the electrolysis with a view to obtaining iron free from hydrogen, the evaporation of the water is a serious difficulty. This is avoided by raising the boiling point of the electrolyte by the addition of salts of metals which are not set free by the electrolysis of their aqueous solutions. Calcium or magnesium chlorides are commonly used.[1]

Zinc.—The electrolytic preparation of the moderately base metal zinc was formerly not possible owing to the corrosion of the anodes of lead, which are the best to use. The attack was traced to impurities in the electrolyte, such as chlorides from the water employed, and after the removal of these it is possible to use a sulphuric acid solution of zinc sulphate with high current density. *Cadmium* is obtained in increasing quantities as a by-product in this process.

Tin.—Tin is the only other metal of this group which is separated on any scale by the electrolytic method. The ordinary metallurgical methods are in use for the working up of tin ores, but the application of the electric current is more advantageous for the recovery of the tin in waste tin plate (sizzle). The trimmings are packed into wide-meshed iron baskets, which are then used as anodes in sodium hydroxide solution. The tin then goes into solution as sodium stannite, Na_2SnO_2, while the iron is not attacked. The tin is deposited as a loose layer on the cathode. Some of the tin, however, is oxidised to the stannic form at the anode, and at the cathode this is more difficult to reduce to the metal than the bivalent form. The disadvantages of the electrolytic method of dealing with this waste product, as compared with the chemical methods (*e.g.* with chlorine), are due to the mechanical difficulties in causing solution at the anode to proceed at a sufficiently rapid rate. Diffusion of the liquid from the wire cage is slow, and the grease and varnish which are often present on the sizzle decrease the rate of solution ; the sodium hydroxide absorbs carbon dioxide during the process and the stannite cannot then be formed. The slimy deposit on the cathode is not convenient for working up, though a firmer deposit can be obtained if a solution of the thiostannite K_2SnS_2 is electrolysed.

A later process, in which a sulphuric acid solution of stannous salts, containing aromatic sulphonic acids (*e.g.* cresol sulphonic acids) and glue, is used as electrolyte, appears to give better results.

Alloys.—When several metals are deposited simultaneously it is possible to produce alloys. As the different metals have a different

[1] See W. E. Hughes, *Monograph on the Electro-Deposition of Iron.* D.S.I.R., 1922.

electrolytic solution pressure there is a tendency for the least base metal to be deposited by itself in the first place. This is avoided by having the baser metals present in higher concentration in the solution. For example, if an equimolecular solution of copper and zinc double cyanides is electrolysed, the brass formed on the cathode contains only one part of zinc to four of copper; if it is desired to make a 1:1 alloy, the solution must be very rich in zinc. It is clear that the solution will become still richer in zinc relatively as the electrolysis proceeds, and this must be corrected by the addition of fresh copper salt. The deposition of the baser metal is in any case due to the local exhaustion of the copper in the electrolyte at the cathode.

It is important to have a fairly dilute solution of the ion to be deposited at the cathode, not only to ensure the deposition of the metal in a smooth coating, but also to permit of the deposition of a baser metal when required. This result is obtained without undue dilution of the liquid by the use of complex compounds of the metal. The solutions of the salts in potassium cyanide, oxalates, ammonia, etc., are commonly employed. A silver solution in KCN contains the compound $KAg(CN)_2$, which gives very few silver ions and retains the silver in the form of the anion $Ag(CN)_2'$. In practice, the low concentration of silver ions is maintained by decomposition of the complex, so that a low but constant concentration of the pure silver ion is kept up. The use of complex compounds permits very different concentrations of the ions of two metals to be present at the same time at the cathode; the one with less tendency to form complexes gives the free ion in greater quantity, so that the concentration of its ions at the cathode remains high.

Sometimes the alloy deposited is a compound and not a mechanical mixture. When this happens the solution pressure of the compound formed cannot be predicted, and very often the metals do not show a selective solubility once they are deposited. Thus copper and tin can be deposited to give an alloy which is a chemical compound. The alloy does not redissolve unless both metals are attacked simultaneously.

Preparation of the Noble Metals

SILVER, GOLD AND THE PLATINUM METALS

The resistance of these metals to the attack of reagents is shown by the frequency with which they are found free in nature. Sometimes they are found alloyed with other metals. The instability of their compounds makes it possible to obtain these metals by the action of heat or of the milder reducing agents, and once they are obtained they form compounds with relative difficulty. Under natural conditions the sulphides are the most stable compounds, and these are often present in pyrites. Silver also occurs as chloride (horn silver), as the special properties of this compound lead to its preservation.

It therefore follows that the winning of these metals is a matter of the working up of the natural reguline masses, of the sulphide ores, and, for silver, of the chloride. They are also frequently recovered from residues resulting from the preparation of base metals.

Gold occurs in the free state, while platinum is usually alloyed with other metals; the quantities of free silver are unimportant. On account of its high specific gravity, gold (and the platinum metals) can be separated from the accompanying sand by elutriation, the best method being to wash with jets of water. Only the larger nuggets are isolated in this way and the more minute particles pass into the gangue and must be recovered by chemical methods.

Amalgamation.—Gold can be extracted direct by amalgamation; the stamped ore is either mixed with mercury or run over amalgamated copper plates, when the gold particles adhere to the plates as an amalgam. The mercury is subsequently distilled off.

When the metal does not occur in the free state the ore must be reduced before amalgamation can be applied. The sulphide ores of silver, for example, are first converted into chloride, from which the silver is liberated by baser metals. When the silver is already present as chloride it can be treated by the copper tank process (pan amalgamation), in which it is treated with mercury in copper vessels. In this way silver amalgam and copper chlorides are formed, the latter being soluble in the concentrated solution of sodium chloride added. The other ores of silver are converted into chloride by roasting with common salt. The roasted mass is then treated with iron borings and water in tubs, or ground in iron pans, when the silver is liberated by the iron. The amalgam is removed and the mercury distilled off in iron retorts— the remaining "plate silver" being then further refined. Another method is to leave the finely ground ore for some months in heaps mixed with salt and then to add copper chloride made from pyrites, with a final treatment with mercury, when the amalgam is worked up in the usual way. The intermediate product in this process is $NaAgCl_2$, which is converted into calomel and silver amalgam by the action of mercury.

Processes involving the Use of Lead.—The amalgamation processes are only applicable to fairly rich ores and to gold ores which are not "rebellious" owing to their content of arsenic and antimony. For these and for the less rich ores the methods employed involve the formation of lead alloys of the precious metal. Silver, indeed, often occurs in conjunction with lead, and must then be extracted from the argentiferous galena or from the work lead obtained therefrom. Further, the baser metals can often be removed by fusing an ore with galena, as they are converted into sulphides and thus removed (*e.g.* iron in platinum ores). Another advantage in the use of lead is the ease with which it can afterwards be removed from the alloy.

O

The silver sulphide in ores is reduced by the addition of lead:
$Ag_2S + Pb \longrightarrow PbS + 2Ag$. The method of working up the lead alloy
depends on whether it is rich or poor in silver. The lead in a rich
work lead is removed by cupellation. This process is carried out on
a porous hearth, on which the metal is fused in an oxidising atmosphere.
Under these conditions only the lead is oxidised, as the silver oxide
is not stable at the temperature of the furnace; the lead oxide is not
miscible with the metal and floats on its surface. The greater quantity
of the litharge is removed and the rest is taken up by the porous hearth.
As the litharge is absorbed, the layer of oxide on the metal becomes
thinner, until finally it disappears altogether and the bright surface of
the silver becomes visible—the flashing of the silver. This refined
silver contains up to 5 per cent. of impurities, and is further purified by
fusion with materials which carry off these impurities into the slag.

Gold ores which cannot be treated by the amalgamation process
directly are treated in a similar way. Platinum ores are fused with
galena and the lead-platinum alloy refined with a flux of glass and lead
oxide to remove sulphur; the osmium and iridium (osmiridium) then
settles to the bottom. The lead-platinum alloy is then remelted in a
furnace lined with lime, and lime is added; the lead is converted into
oxide and is soaked up by the lime, and some of the other impurities
are volatilised or converted into oxides and taken up by the lime (gold,
palladium, osmium and base metals). This method can also be used
for working up platinum residues which contain impurities (e.g. sulphur,
silicon, carbon, phosphorus and arsenic), which cause brittleness or lack
of inertness to reagents.

It does not pay to work up poor argentiferous lead by cupellation
without a previous concentration of the silver in some other way. Two
methods are in use: in the Pattinson process the alloy is allowed to
crystallise, when pure lead appears first, and the silver-lead eutectic
(Ag, 2·25 per cent., m.pt. 303°) remains liquid; while in the Parkes
process a third metal (zinc) is added to give an alloy of higher melting
point, which separates out first. The rich lead from the Pattinson
process is further purified by blowing steam through it, which not only
aids the mechanical separation of the lead, but also oxidises the free zinc
and antimony which are thus brought to the surface (Rozan process).

Molten zinc and lead are only partially miscible, so that in the
Parkes process the silver is distributed between the two liquid
layers. The zinc layer takes up the greater part of the silver;
but a single treatment does not remove the silver entirely. It is
necessary to remelt the residue with more zinc after removing
the first zinc crusts, and to repeat this process several times.
As the silver content diminishes in accordance with the partition
law with each extraction, it is usual to separate silver only from
the first rich fractions, the later crystallisations being used to work

up fresh batches of argentiferous lead. The Parkes process, when applied several times to the lead, reduces the silver content to 0·0005 per cent., while the residual lead also contains 0·5 per cent. of zinc, which can be removed by the injection of steam as described above. The very first fractions contain the gold, which is more readily obtained if only a little zinc is used for the original treatment. The zinc is distilled from the crusts which separate in the Parkes process, and the residue cupelled to obtain the silver and gold.

Wet Processes.—Other processes involving the precipitation of these metals from aqueous solutions are in use. Silver is usually precipitated by the addition of baser metals, while for gold there is a wide choice of reducing agents. On the large scale, ferrous sulphate and sulphur dioxide are commonly employed, while for more delicate reductions formic, oxalic and arsenious acids, acid stannous chloride, alkaline hydrogen peroxide, formaldehyde and many other substances can be used. The silver or gold is first converted into a salt such as the chloride, double cyanide or thiosulphate.

Pyrites containing gold can be treated by roasting and direct treatment with chlorine and water (Plattner's chlorination process). The solution is precipitated with hydrogen sulphide, the sulphide dissolved in *aqua regia*, and ferrous sulphate added, when the gold is precipitated quantitatively and the other metals remain in solution. When silver is chlorinated the product is insoluble. In Augustin's process the silver ore is roasted with common salt, when silver chloride is produced, which is leached out with strong brine as $NaAgCl_2$; the silver is precipitated from this solution by the addition of copper. Alternatively, the silver sulphate itself may be washed out and the metal precipitated by copper from this solution (Ziervogel). Other methods are to extract the ore with thiosulphate after a chlorinating roast, and then to precipitate in the first place with sodium sulphide; extraction with potassium cyanide, again, has the advantage that the solution obtained can be used direct for the electrolytic separation described below, but it is necessary to avoid the formation of thiocyanates from ores which contain sulphur. Gold can be precipitated from the cyanide solution with zinc, preferably after adding a little lead acetate, as it is found that the gold is deposited more rapidly on the lead-coated zinc.

Electrolytic Processes.—As the noble metals are so easily obtained pure by reduction methods, the application of electrolytic methods has been rather limited. They are in fact used only for refining, as in the removal of silver from gold, or in the elimination of traces of platinum from the same metal.

In the electrolytic refining of gold, either a chloride solution or a cyanide solution is employed. When a chloride solution is used the platinum and palladium go into solution from the anode and are deposited on the cathode with the gold when their

concentrations exceed 60 g. of platinum and 5 g. of palladium per litre. The solution must then be removed from the electrolytic cell and the metals separated chemically. This is done by precipitating the gold with sulphurous acid or ferrous sulphate and the platinum as $(NH_4)_2PtCl_6$ by adding ammonium chloride. The palladous chloride remaining in the solution ($PdCl_2$) is obtained by evaporating if necessary to a small bulk or to dryness and dissolving the residue in ammonia ; on adding hydrochloric acid to the solution it is precipitated as $[Pd(NH_3)_2Cl_2]$.

The other platinum metals are found in the anode slimes, together with the silver, which is converted into silver chloride. If there is much silver in the metal of the anode (more than 6 per cent.) the silver chloride remains on the anode and must be scraped off from time to time or the electrolysis comes to a standstill ; but it is better to perforate the layer of silver chloride by superimposing an alternating current on the direct current used for the electrolysis, when the chloride peels off and falls into the slimes.

There are several difficulties in causing the solution of the gold at the anode ; the metal becomes passive and, instead of the gold being dissolved, oxygen is given off. This can be avoided in two ways : by raising the temperature and by addition of free hydrochloric acid. There is then a danger that chlorine will be given off at the anode instead of oxygen, but this does not happen if the current density is kept low. A further difficulty is the tendency for the aurous ions $Au^{\cdot}$ to form free gold and auric ions, $Au^{\cdot\cdot\cdot}$, thus : $3Au^{\cdot} \rightleftharpoons Au^{\cdot\cdot\cdot} + 2Au$. The metallic gold produced in this way falls out as a slime, and the solution tends to become exhausted.

This reaction can, however, be held up to some extent ; the equilibrium between the aurous and auric ions must not be reached by the time the anode liquid has arrived at the cathode. The actual reaction at the cathode involves the reduction of more or less $Au^{\cdot}$ ions in place of $Au^{\cdot\cdot\cdot}$ ions, according to the condition of the electrolyte at the cathode.

The electrolysis of cyanide solutions is of greater technical importance than that of the chloride solutions. These solutions are obtained in the extraction of gold ores by cyanide ; the finely powdered ore is treated with potassium or sodium cyanide of 0.1-1.0 per cent. concentration and the mixture aerated. Under these conditions the cyanions form a complex $[Au(CN)_2]'$, and the oxygen of the air is reduced to hydrogen peroxide.[1] The hydrogen is derived from the water, as hydroxyl ions are set free. The somewhat complex reaction is as follows :

$$2Au + 4CN' + 2H^{\cdot} + O_2 = 2Au(CN)_2' + H_2O_2.$$
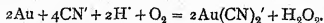
This is followed by a further reaction in which the H_2O_2 acts as the oxidising agent :

$$2Au + 4(CN)' + H_2O_2 = 2Au(CN)_2' + 2OH'.$$
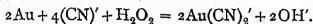
The solution thus becomes strongly alkaline. The cyanide solution is only electrolysed till the bulk of the gold is deposited, as the complete removal of the gold needs a great expenditure of current, and much

[1] Bodländer, Z. angew. Chem., 1896, 10, 583.

oxygen is evolved at the anode. As the cyanide is left in solution the liquid can be used for a further extraction of ore.

The Parting of Silver and Gold.—Among the methods used for this purpose may be mentioned that of boiling the regulus with concentrated sulphuric acid, when the silver is dissolved and the gold powder left contains only 0·002 per cent. of silver. This method can be used for all alloys, while the corresponding treatment with nitric acid (parting acid) is applicable only to alloys rich in silver, so that more silver must sometimes be added to the metal before the separation is attempted. The alloy frequently used is one containing one part of gold to three of silver (quartation). The gold thus obtained is refined by fusion with borax and nitre, but it still retains a little silver.

Platinum Metals.—The separation of the various metals of the platinum group from the ores which contain them in small quantities, together with much platinum, can be carried out by various methods (see also pp. 210 and 212).

Over half the world's consumption of Pt metals is derived from the residues remaining after the removal of Ni by the carbonyl process [1] or from anode slimes obtained during the electrolytic purification of nickel and copper (see p. 199). The latter material, after treatment with acids, contains about 50 per cent. of Pt metals, while the former contains the following approximate percentages: Ag, 15; Pt, 2; Pd, 2; Au, 0·6; Rh, 0·2; Ru, 0·2; Ir, 0·04; an initial concentration by smelting with litharge and sodium carbonate is necessary for the poorer concentrates. The precious metals collect in the lead, and the slag contains the silica and base metals, together with sodium sulphate, formed from lead sulphate present to the extent of 50 per cent in the slimes.

The lead ingots obtained are cupelled to remove most of the lead as litharge and the resulting alloy, containing some 80 per cent. of precious metals, is parted with boiling conc. sulphuric acid. This removes most of the Ag and a third of the Pd as sulphates. The residue is treated with *aqua regia*, Pt, Pd, and Au dissolving completely as chlorides; these are precipitated as Au, $(NH_4)_2PtCl_6$ and $[Pd(NH_3)_2Cl_2]$ by the reactions given on p. 212. The gold is purified electrolytically, the other metals by repeating the precipitation, after which the complexes are ignited to metals.

Rh, Ru, Ir and only a minute trace of osmium are separated from the residues after an initial concentration by smelting with litharge and cupellation. Au, Pt and Pd are dissolved from the alloy in nitric acid, and Rh is extracted from the residue by fusion with $NaHSO_4$ and purified as described by Gilchrist and Wichers.[2]

[1] Atkinson and Raper, *Industrial Chemist*, 1936, 12, 438; Johnson and Atkinson, *ibid.*, 1937, 13, 223. Dale, "The Precious Metals," *Institute of Chemistry*, 1941.
[2] *J. Amer. Chem. Soc.*, 1935, 57, 2565.

The insoluble residue is fused with KOH and KNO_3 forming potassium ruthenate (and osmate), which is separated from insoluble iridium material, and distilled in a current of Cl. The volatile tetroxides are separated essentially as described below. The remaining iridium material is soluble in *aqua regia*; from the solution ammonium iridichloride is precipitated and ignited to metal.

For the separation of the platinum metals,[1] the powder is fused with sodium peroxide ; the liquor resulting from the treatment of the mass with water is distilled in a current of chlorine. Osmium and ruthenium are volatilised as tetroxides, which are condensed in hydrochloric acid. This distillate is again distilled in a current of air, when ruthenium tetroxide is reduced to trichloride by the hot acid, while osmium tetroxide distils unchanged and is collected in alcoholic sodium hydroxide, and is thus converted into sodium osmate. The ruthenium solution is then precipitated with magnesium ; and the osmate solution with aluminium foil or with an alkali sulphide, and the sulphide precipitate ignited to metal in a carbon crucible.

The other platinum metals remaining in the solution from the distillation are converted into chlorides by evaporation with *aqua regia* ; this solution is precipitated with ammonium chloride. The precipitate consists of ammonium chloroplatinate and chloroiridate : it is ignited and the resulting mixed metals fused with lead. The lead alloy is decomposed with nitric acid and the residual sponge digested with *aqua regia* ; iridium remains behind while platinum dissolves and is recovered by reprecipitation with ammonium chloride and ignition of the precipitate.

The filtrate from platinum and iridium contains palladium and rhodium, which are separated by adding mercuric cyanide ; the precipitate, $Pd(CN)_2$, on ignition leaves metallic palladium, and the rhodium in the filtrate is precipitated as metal by magnesium.

[1] The translator is indebted to Dr W. R. Schoeller for the account of this separation.

II. HALOGEN COMPOUNDS

CHAPTER VIII

HYDROGEN COMPOUNDS OF THE HALOGENS

Halogen hydracids—Preparation—Properties—Applications of the phase rule

Formation

1. *Synthesis from the Halogen and Hydrogen.*—The synthesis of these hydrides takes place more readily the greater the affinity of the halogen for hydrogen. The heat of formation of the acid may be taken as a measure of the affinity, as has already been explained on p. 160, where the equilibrium $H + X \rightleftharpoons HX$ is quoted. This equilibrium is independent of pressure, for in the reaction $H_2 + Cl_2 \longrightarrow 2HCl$ the number of molecules and hence the volume is unaltered. The equilibrium is, however, affected by variation in temperature, a rise in temperature favouring the decomposition of the acid. This occurs most readily with hydriodic acid, thus:

600°	700°	800° T.	
19	22	25	per cent. decomposed

Hydrobromic acid is more stable—

303°	900°	1381°	2000° T.
1.23×10^{-7}	7.2×10^{-2}	0.81	3.40 per cent. decomposed

while hydrochloric acid is only slightly decomposed at high temperatures—

303°	1810°	4000° T.
1.3×10^{-14}	0.22	10 per cent. decomposed

The thermal decomposition of hydrofluoric acid has not yet been investigated.

These figures also indicate the extent of combination at various temperatures. Thus iodine and hydrogen combine to the extent of 75 per cent. at 500°, while the combination of chlorine is practically complete at that temperature. Fluorine and hydrogen combine instantaneously and explosively under all conditions—even in the dark at −252°. Chlorine and hydrogen detonate like oxygen and

hydrogen; this reaction must be started by exposure to light or by heating. In diffused daylight, or at lower temperatures, or in the presence of suitable catalysts (*e.g.* carbon), the combination occurs at a measurable rate. Ultra-violet light is the most active, and as light causes the dissociation of the chlorine molecule into its atoms, it is probable that the reaction does not take place between the molecules of the reactants, but that the decomposition of the chlorine molecules is a necessary preliminary. The rate of reaction, when proceeding quietly, is not that of a double decomposition between *two* substances, but corresponds more nearly, though not accurately, to that of a decomposition of one of the reacting substances. The velocity is independent of the hydrogen concentration but is proportional to that of the chlorine. It can therefore be supposed that it is the velocity of the reaction $Cl_2 \longrightarrow 2Cl$ which is measured, while the consecutive reaction between Cl and H_2 proceeds with great rapidity. The reaction between bromine and hydrogen takes place in a similar manner. The action of ultra-violet light is thus easily explained by its accelerating effect on the primary process of decomposition of the chlorine molecules. Coehn and Wassiliewa[1] have shown that exposure to ultra-violet light has the same effect as heating to 1500°.

Taylor and Marshall[2] have shown that it is extremely probable that the light reaction merely gives the impulse for a series of reactions, in which the Cl atom displaces a H atom from H_2, when this H atom in turn attacks a Cl_2 molecule thus:

I. $Cl_2 \xrightarrow{\text{light}} 2Cl$; II. $Cl + H_2 \longrightarrow HCl + H$; III. $H + Cl_2 \longrightarrow HCl + Cl$,
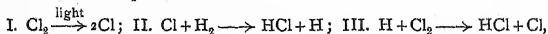
for when atomic hydrogen is introduced into chlorine, more HCl is formed than the theoretical yield.

The essential correctness of this mechanism has been confirmed by studying the interaction of deuterium and chlorine; here the reactions are $Cl + D_2 \longrightarrow DCl + D$; $D + Cl_2 \longrightarrow DCl + Cl$; the second stage will proceed with approximately equal velocities for atomic H or D, but the first stage involving D_2 should proceed at about one-third of the rate of the H_2 reaction; experimental results agree closely with theoretical requirements.[3]

The presence of a certain quantity of water was long supposed to be essential for the combination of the gases, but work by Allmand and Bodenstein seems to indicate that water is not essential. However, the combination of dry chlorine and hydrogen at 450° proceeds only to the extent of 80 per cent. in ten minutes, while only 30 per cent. of the mixture is found to be combined after exposure to sunlight at room

[1] *Ber.,* 1909, 42, 3183.
[2] *Nature,* 1923, 112, 937 ; *J. Phys. Chem.,* 1925, 29, 842.
[3] L. and A. Farkas, *Naturwiss,* 1934, 22, 218.

temperature for three days. When damp, the gases explode at once on illumination or on heating in the dark to about 250°. The reaction is retarded in darkness by certain negative catalysts, *e.g.* ozone, nitric oxide or traces of ammonia; on exposure to light they are rendered innocuous by reaction with the chlorine. It has been known for a long time that chlorine which has previously been exposed to light reacts more readily with hydrogen than without this treatment.[1] This is probably due to the removal of inhibiting substances, and not to alteration in the state of the chlorine.

The formation of hydrobromic acid is also promoted by light, but no such effect has been observed with hydrogen iodide.

Hydrogen chloride can also be prepared by bringing a jet of burning hydrogen into chlorine, when it continues to burn, or the two gases can be fed to a blowpipe similar to the oxy-hydrogen blowpipe. In the synthesis on a large scale a slight excess of hydrogen is desirable. The formation of hydrogen bromide is best carried out by allowing hydrogen to pass slowly over warm bromine, and then passing the hydrogen, thus saturated with bromine vapour, over a heated solid contact substance such as asbestos or pumice, which are more effective if platinised. The reaction proceeds smoothly, but the preparation of hydrogen iodide in this way is ineffectual, as the equilibrium mixture at the ordinary temperature of reaction contains considerable quantities of the free elements.

2. *Action of hydrogen on a halogen compound, or of a halogen on a hydrogen compound.*

The reduction of metal halides by hydrogen is easiest with fluorides and most difficult with iodides; this is applied in analysis, for when silver iodide is heated to a red heat in a stream of hydrogen it is not reduced, while silver chloride is reduced readily.

DF has been prepared by heating AgF in a stream of D_2; HF was similarly prepared; DF was found to boil at 18·81° and HF at 20·07°.[2]

The action of halogens on hydrogen compounds is of greater importance, and, in agreement with the decrease in affinity with increasing atomic weight, is most vigorous when hydrogen fluoride is the product, and least so when hydriodic acid is formed. These reactions are also reversible, but the position of equilibrium is very near a complete reaction. One which has been much studied is that between chlorine and water (*cf.* the Deacon process, p. 166):

$$2Cl_2 + 2H_2O \rightleftharpoons 4HCl + O_2.$$
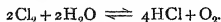
The reaction between fluorine and water is practically complete at the ordinary temperature; oxygen is set free, partly as ozone. Any considerable formation of hydrogen iodide from iodine and water is

[1] See also *Ann. Rep. Chem. Soc.*, 1925, **22**, 333 *et seq.*
[2] Claussen and Hildebrand, *J. Amer. Ch*

scarcely to be expected. The action of the more negative halogens on hydrogen compounds other than water is also invariably more energetic, as is seen most easily when different halogens compete for an insufficient quantity of hydrogen—the halogen of highest atomic weight is left free.

The undoubted reversibility of the reaction $Cl + HBr \rightleftharpoons HCl + Br$ is not effective, owing to the great difference in electro-affinity of the halogens, and is only seen when the affinities of the elements competing for the hydrogen are more similar. For example, it can be studied in reactions in which oxygen and chlorine compete for hydrogen (see above), or in the equilibrium between iodine and hydrogen sulphide, the iodine and sulphur being closely related in electro-affinity. With excess of sulphuretted hydrogen, hydriodic acid is formed, and the acid can conveniently be prepared by passing a stream of the gas into a suspension of iodine in water. The precipitation of sulphur ceases when the liquid is decolorised. But this complete formation of hydriodic acid in aqueous solution is due to the almost negligible solubility of sulphur, for in the gaseous state the equilibrium can be shown to exist up to 500°.[1]

As may be expected, the reaction between hydrogen sulphide and the other halogens is more energetic. With fluorine, the mixture of gases ignites spontaneously, and if excess of fluorine is present it combines with the liberated sulphur to form a sulphur fluoride.

The action of the halogens on ammonia or hydrazine is similar, the halogen acid being produced ; and here again when excess of halogen is present a halogen nitride is formed. The halogens similarly react with hydrocarbons forming halogen derivatives of the hydrocarbon and the halogen hydracid, $e.g.$ $CH_4 + 3Cl_2 \longrightarrow CHCl_3 + 3HCl$. Fluorine and chlorine often react with great energy ; for instance, with methane the mixture catches fire. With less simple hydrocarbons the reaction is slower, and a regular stream of hydrogen bromide can be obtained by the action of bromine on paraffin, benzene, naphthalene, etc.

3. *Decomposition of halogen compounds by water* (hydrolysis) is a method frequently employed for the preparation of the halogen hydracids. Halides of either metals or non-metals can be used. The hydrolysis proceeds as follows :

$$MX + H_2O \rightleftharpoons M(OH) + HX,$$
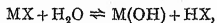
and goes to completion when the halogen hydride escapes as a gas from the medium in which the reaction takes place. The completion of the reaction is thus not favoured by the presence of large quantities of water, in which the acid remains dissolved. But if the acid is continually removed from the reaction mixture the decomposition is complete, even when the equilibrium concentration of the acid is low. These conditions are fulfilled when liquid water is absent, and

[1] Berthelot, *Compt. rend.*, 1878, 87, 667.

the reaction is carried out in a stream of water vapour which carries off the acid as fast as it is formed. Thus in a technical process for the production of hydrochloric acid steam is blown over heated magnesium chloride. Lewis, Macdonald and Schutz[1] prepared DCl by passing D_2O over $MgCl_2$ at 600°; they found m.pt. of DC to be 158·2° T. and b.pt. 191·5° T.

These conditions are also fulfilled in the hydrolysis of many non-metallic halides. Thus when water is dropped on to phosphorus tri-chloride: $PCl_3 + 3H_2O \rightleftharpoons P(OH)_3 + 3HCl$, as the hydrochloric acid is also only slightly soluble in these liquids, it is continuously evolved and the reaction proceeds practically to completion. The method is employed with advantage in the preparation of hydrobromic and hydriodic acids; it is not essential to prepare the phosphorus halides, for the reaction occurs when, for example, bromine is dropped on to a mixture of phosphorus and a little water, or when a mixture of iodine and phosphorus is wetted. In the latter reaction it is necessary to have an excess of iodine present to prevent the formation of phosphonium iodide. The gaseous halogen acid can be absorbed in water if required.

4. *Decomposition of Halides with less volatile Acids.*—When a solution which contains halogen ions is treated with one containing hydrogen ions, halogen acids are formed by the reversible reaction

$$H^{\cdot} + Cl' \rightleftharpoons HCl.$$
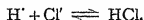
This method is therefore applicable to the preparation of these acids when they are insoluble in the reaction mixture, and are consequently evolved as gases, so that the formation of the acid is continued to maintain the equilibrium (*e.g.* in the decomposition of solid sodium chloride with concentrated sulphuric acid). In the presence of larger quantities of water the production of halogen acid ceases, and the reaction comes to a standstill in the position of equilibrium. The acids which are useful for this preparation are therefore anhydrous acids, such as sulphuric and phosphoric acids, which neither dissolve nor dissociate the halogen acid.

The displacement of a halogen acid from a halide has but little relation to the strength of the acid added, as it depends much more on the greater volatility of the acid displaced. An acid can generally be displaced from its salts by another acid of higher boiling point. Even the relatively feeble acids, boric and silicic, displace the strongest acids from their salts owing to their low volatility. Thus, when sulphates are heated to a red heat with silica, a silicate is formed in spite of the reversibility of the reaction: $K_2SO_4 + SiO_2 \rightleftharpoons K_2SiO_3 + SO_3$, which favours the formation of sulphate; for owing to the low solubility of the sulphur trioxide in the reaction mixture and to its volatility, only a small quantity remains behind. This small quantity is continuously reproduced to maintain the equilibrium, and in this way the sulphate is completely decomposed.

[1] *J. Amer. Chem. Soc.*, 1934, 56, 494.

Hydrofluoric acid is made in this way from fluorspar (CaF_2) or cryolite (Na_3AlF_6), by heating with concentrated sulphuric acid in retorts of lead, iron, or better, of copper, since glass is attacked by the acid produced. Hydrochloric acid is similarly made by decomposing common salt with sulphuric acid: the salt is merely mixed with a little acid, and then on adding more acid gradually a regular stream of hydrogen chloride is evolved. Only the bisulphate is formed at the ordinary temperature: $NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$, but, on heating, the bisulphate reacts with a second molecule of salt: $NaCl + NaHSO_4 \longrightarrow Na_2SO_4 + HCl$. By using large pieces of sal-ammoniac in a Kipp's apparatus, hydrogen chloride can be obtained in any desired quantity by the same reaction.

The preparation of hydrobromic or hydriodic acids by this method is unsuccessful owing to the reducing action of these acids on the sulphuric acid; so that, instead of hydriodic acid, free iodine, together with sulphuretted hydrogen, sulphur and sulphur dioxide, is obtained. Phosphoric acid, which is not so easily reduced, can be employed, when the action proceeds in the desired manner. Gaseous hydriodic acid can likewise be obtained by dehydrating the aqueous solution with phosphorus pentoxide.

5. *Heating of Acid Halogen Salts.*—All halogen acids form acid salts corresponding to polymerised forms. Hydrofluoric acid forms these compounds most readily, and the acid potassium salt, KHF_2, is decomposed into KF and HF on heating. This reaction is of importance inasmuch as it can be carried out in absence of water, and so serves for the preparation of the anhydrous acid.

Physical Properties.—Hydrogen chloride, bromide and iodide are colourless gases, liquefiable at low temperatures and freezing to colourless crystalline solids on further cooling. The melting and boiling points of the halogen acids are as follows:

	HF	HCl	HBr	HI
Melting point .	$-83°$	$-114°$	$-87°$	$-52°$
Boiling point .	$+19.4°$	$-85°$	$-66°$	$-36°$

The boiling points of HBr and DBr, and of HI and DI are practically identical; the boiling point of DF is about 1° lower than that of HF, whereas HCl boils nearly 3.5° higher than DCl.

The melting and boiling points rise in this series from hydrochloric to hydriodic acid, as is often the case with similar compounds in series of increasing molecular weight. Hydrofluoric acid, however, is an exception to the gradual variation of properties, its abnormally high boiling point indicating a difference in constitution. Its density in the gaseous state shows that its molecular weight is much greater than corresponds to the simple formula, whereas that of the other halogen acids approximates closely to that required by the formula HX.

Hydrofluoric acid is therefore polymerised, and has in the liquid state a molecular weight corresponding to the formula $(HF)_6$; in the gaseous state these polymerised molecules persist in equilibrium with HF molecules at temperatures just above the boiling point. Instead of the theoretical value for the molecular weight (20·02), the values obtained from the density are:

Temperature .	.	26·4	36·3	47·3	69·4	88·1°
Molecular weight	.	51·2	32·2	23·7	21·0	20·6

the value being more than three times the theoretical just above the boiling point. The abnormal boiling point is thus easily explained. The polymerisation is not noticeable in aqueous solution, as dilution causes dissociation of the complex molecule in the same way as rise in temperature; this dissociation is assisted also by the affinity of the water for the HF molecules. The principle of Le Chatelier indicates that dilution of any sort tends to an increase in the number of molecules.

The density of the liquefied acids also shows an increase with rising molecular weight:

$(HF)_n$	HCl	HBr	HI
$d_{11°}$ 0·99	$d_{-81°}$ 1·18	$d_{-60°}$ 2·16	$d_{-88°}$ 2·79.

The density of hydrogen fluoride is not far out of the general series, but is, however, conspicuously near to that of hydrogen chloride on account of its polymerisation. Even in the liquid state hydrogen iodide is unimolecular, while the condition of hydrogen chloride may be represented by $(HCl)_{1.5}$. This polymerisation, which is considered to be due to the formation of a resonance-hybrid, is dealt with on p. 347.

The liquefied acids are but poor conductors of electricity; their conductivity is of the same order as that of pure water. In aqueous solution, however, hydrochloric, hydrobromic and hydriodic acids are strongly ionised.

The liquefied acids are in general not good solvents for inorganic substances; but phosphorus halides, hydrogen sulphide and sulphur dioxide are miscible with them in all proportions. The solution of certain organic substances, which contain oxygen, nitrogen or sulphur, in the anhydrous acids takes place with evolution of heat and solid products can be isolated, particularly from ethers. The compounds with hydriodic acid are the most stable, but the melting points of all these compounds are below 0°. Combination would appear to occur by the linking of the oxygen (nitrogen, sulphur) atom to the molecule of hydrogen iodide. Formerly the quadrivalency of oxygen was assumed in such compounds, but they are best formulated on the basis of the electronic theory, as follows:

$$\left[\begin{array}{c} CH_3 \\ CH_3 \end{array} \!\!\!\! > \overset{+}{O} \overset{=}{=} H \right]^{-} I^8 \quad \text{or} \quad \left[(CH_3)_2 O \longrightarrow H \right]^{+} I^-$$
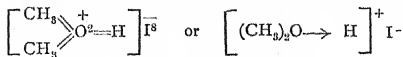
Acids occupy a special position among chemical compounds, as the hydrogen ion has no electrons but consists of a bare nucleus. The transference of the solitary electron of the H atom to the halogen atom completes the outer level of eight of the latter, thus:

$$H : \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} :$$

The compound thus formed can be regarded as polar provided the H is not considered to be attached to the Cl atom by any particular electron pair; it can then be written H˙Cl'. On the other hand, the union can be regarded as non-polar, if the attachment is by means of one particular pair of electrons, the two being then shared between the H and Cl atoms. Arguments based on thermochemical data, internuclear distance and dipole measurements indicate that in the normal HCl gas molecule, the H—Cl bond is about 17 per cent. ionic, the remaining bond energy arising from the covalent character of the bond and from deformation. If, however, the H is hydrated, the polar union is the only one possible thus: $H˙ + H_2O \longrightarrow [H_3O]'$, for here eight electrons are present, thus forming a complete octet, and no question of sharing arises. Hence $Cl'[H_3O]˙$ is ionised as follows:

$$\left[: \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} : \right]^{-} \qquad \left[\begin{array}{c} H \\ : \overset{\cdot\cdot}{O} : H \\ H \end{array} \right]^{+}$$
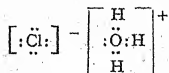
It is extremely probable on general grounds that the naked hydrogen nucleus would be prone to hydration, and the work of A. Hantzsch[1] indicates that this process is of extreme importance, as the acidic properties depend on it. According to this author, all acids in the pure undiluted state have a non-polar structure. Thus the halogen hydrides, for instance, can be regarded as the first members of the series of non-polar alkyl halides: HCl; CH_3Cl; C_2H_5Cl, etc., as all their physical properties, particularly the optical ones, make them appear as of the same nature as the alkyl halides. When the hydrides are dissolved in water or converted into salts, the properties are fundamentally changed owing to hydration. The hydroxonium compounds thus obtained are formed by the union of the hydrogen ion with a water molecule. Thus the non-polar HCl forms the polar hydroxonium chloride: $[ClH] + H_2O \longrightarrow Cl'H_3O˙$. Hantzsch suggests that no hydrogen ions are formed at all but only hydroxonium ions, probably solvated to an even greater extent than this formula would indicate. Further, the strength of an acid should be measured, not by its dissociation in aqueous solution, but by its ability to form salts. Salt formation can proceed either by the addition of unsaturated compounds, such as water, ammonia or ether, or by the replacement of the hydrogen by

[1] Z. physikal. Chem., 1928, 134, 406.

metals; actually, the series of acids in order of strength obtained on
the basis of salt formation is not very different from that derived from
the dissociation in aqueous solution, the first being:

$$HClO_4 > R \cdot SO_3H > HI > HBr > HCl > HNO_3,$$

while the second gives:

$$HClO_4 > HI > HBr > HNO_3 > HCl > H_2SO_4.$$
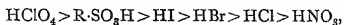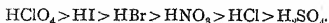
The displacement of the series in aqueous solution appears to be due
to a levelling off due to the addition of water—the formation of
hydroxonium salts. Hantzsch calls substances which are not acids
themselves, but which become acids when combined with other
substances, pseudoacids. The general theory of these substances is
discussed on p. 360.

The solubility of the halogen hydrides in water is high, about 500
volumes of the gaseous acids being dissolved by one volume of water.
When the acid solution is warmed, the vapour formed is richer in acid
than the liquid; and if the heating is continued to boiling, the boiling
point rises with decrease in the acid concentration until a point is
reached when the vapour contains the same relative concentration
of acid as the liquid. The composition of this liquid, and therefore
its boiling point, does not alter with loss of vapour and it distils to
the last drop, with the same boiling point and composition. Starting
with a more dilute acid, a vapour containing less acid than the liquid
is first given off, with a consequent increase in the concentration in
the liquid. The boiling point rises to a maximum, when the liquid
has the same boiling point and composition as that obtained from the
concentrated acid. This liquid also distils unchanged. Although
halogen acids of constant boiling point are thus obtained, there is
no question of a compound being formed with the water.

The following table shows the constant boiling points of the halogen
acids under atmospheric pressure, and the density, percentage com-
position and ratio of water molecules to acid molecules in the dis-
tillates:

	HF	HCl	HBr	HI
Constant boiling point .	120°	110°	126°	127°
Density	1·14	1·10	1·49	1·70
Per cent. acid . . .	35·37	20·24	47	57
Ratio	2	8	5	2·5

The effect of alteration of the pressure on the composition of constant
boiling hydrochloric acid is shown below:

Pressure . . .	50	500	760	2500 mm.
Per cent. HCl . .	23·2	21·1	20·24	18·0

A simple practical rule for calculating the approximate percentage of hydrochloric
acid in any aqueous solution of the acid is to multiply the decimal fraction in the

density by 2 ; thus, an acid of density 1·10 contains 20 per cent. (actually 20·2 per cent.), and one of density 1·21, the strongest acid that is stable at ordinary temperatures and pressures, contains 42 per cent. (accurately, 41·7 per cent.) of HCL.

Chemical Properties.—The chemical behaviour of the anhydrous hydrogen halides is naturally different from that of their aqueous solutions, as acidic properties are manifested only in solution. The displacement of hydrogen by metals is almost completely inhibited by the absence of water. Even the alkali metals react with difficulty with the liquid anhydrous hydrogen halides, mostly owing to the absence of ionisation, and to the consequent insolubility of the salts produced in the liquid ; generally, polar substances dissolve in polar solvents and non-polar substances in non-polar solvents. It is possible that the slight reaction which does take place would not occur if it were possible to remove the last traces of water.

In the same way, carbonates are not dissolved by the anhydrous acids, nor are chromates reduced. Solutions of the hydracids in non-dissociating solvents, such as benzene and toluene, which dissolve hydrogen chloride readily, have no action on metals or carbonates, thus showing that this indifference is due to lack of ionisation. When water is one of the products of the reaction, the rate of reaction gradually increases, even though it may be slow to begin with. Thus oxides react with dry hydrofluoric acid at high temperatures with formation of fluorides, $MO + 2HF \longrightarrow MF_2 + H_2O$, as water is formed, and oxides or hydroxides of non-metals react in a similar way : thus boric acid gives BF_3 or HBF_4, silicic acid gives SiF_4 or H_2SiF_6, and the oxides of the metallic members of Groups IV, V and VI of the periodic system (Ti, V, Nb, Ta, Mo, W) react in a similar way.

The reactions of the halogen acids in aqueous solution are conditioned by their acidic character and by their reducing action. As acids, they dissolve all the metals with a greater electrolytic solution pressure than hydrogen ; more electronegative metals are attacked if an oxidising agent is present. Thus, antimony and even mercury will dissolve in hydrochloric acid if air is not excluded, and, of course, still more readily if an energetic oxidising agent such as nitric acid is added. Aqueous hydrofluoric acid slowly attacks all metals except platinum and gold.

The reducing action of the halogen acids increases with rising atomic weight of the halogen (see p. 163 *et seq.*), being most marked with hydriodic and non-existent with hydrofluoric acid. The reaction of the halogen acids with sulphuric acid (p. 219) is typical of the varied difficulty of oxidising them. To remove the hydrogen from hydrochloric acid definite oxidising agents are necessary, such as peroxides, per-acids, MnO_2, PbO_2, CrO_3, or other higher metallic oxides, or compounds with easily available oxygen like hypochlorous or nitric acids. The great difficulty of preparing fluorine indicates the extreme resistance of hydrofluoric acid to oxidation.

Hydrates and Pseudo-hydrates.—The property of the acids of fuming in moist air is due to their solutions having a lower vapour pressure than that of the pure solvent. When the acid vapour comes in contact with air which is highly saturated with water vapour, a solution is formed which is liquid at the ordinary temperature. As the system with the lowest vapour pressure tends to be formed these solutions appear in fine drops as a fume.

At low temperatures the compounds of the halogen acids with water are crystalline solids. Those with 1, 2 and 3 molecules of water have been prepared.

The method of investigating chemical compounds by a systematic study of the freezing points of mixtures is known as thermal analysis. It has been applied with con-siderable success in investigating the compounds of the metals with one another. This will be referred to later on p. 865.

The freezing point of H_2O——HCl mixtures may be considered as an ex-ample at this point (Fig. 30). The percentages are expressed as weights and not as molecules of HCl. Between the freezing point of water (A) and that of the highest hydrate (the trihydrate), there is a eutectic at the low temperature

FIG. 30.—The system H_2O——HCl.

B. The eutectic between tri- and dihydrate (C) as well as that between the di- and monohydrate (D) is less distinct; while that between the monohydrate and pure HCl cannot be seen here. If one attempts to obtain it, the mixture separates into two layers—a solution of HCl in H_2O and one of H_2O in HCl—which are non-miscible. The two lower hydrates can be obtained only under pressure.
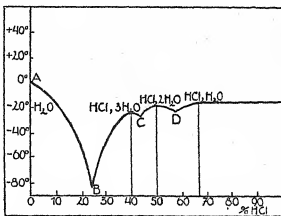
Roozeboom[1] applied the phase rule of Gibbs[2] to the examination of the system HBr—H_2O. It contains two chemical substances, and has therefore no degree of freedom if these substances exist in four phases, but is univariant if only three phases are present. The accompanying diagram shows the phases which exist under different conditions of temperature and pressure.

The ordinates (p) give the pressure, the abscissae (t) the temperature. When the pressure is raised at constant temperature, more HBr dissolves, provided there is enough in the gas space. The quantity of HBr in solution is therefore greater towards the top of the diagram.

Let us first consider curve AFB. This shows the limit of existence of the dihydrate in equilibrium with its saturated solution and vapour. If the temperature is raised at constant pressure the dihydrate melts; if the temperature is lowered the

[1] *Z. physikal. Chem.*, 1888, **2**, 499.
[2] See van 't Hoff, *Ber.*, 1902, **35**, 4252.

P

dihydrate crystallises out. The relations between temperature and the vapour pressure in this system are somewhat complex. On the branch BF the vapour pressure decreases with rise of temperature, owing to the diminished solubility of the HBr; while on the branch AF the pressure increases with temperature in the usual way. This effect is due to the solution below F being poorer in HBr than the dihydrate; at F the composition is the same, and above F the solution is the richer in HBr. When dihydrate separates out along curve AF the solution becomes correspondingly weaker in HBr, so that the temperature need only be lowered slightly for more dihydrate to separate out. But if the dihydrate separates out along the curve BF the solution becomes richer in HBr, since it originally contained more of the acid than corresponded to the dihydrate. The excess of HBr can only be taken up when the pressure is increased or the temperature lowered. Thus for a certain
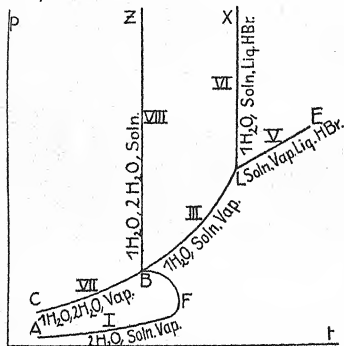
FIG. 31.—The system HBr——H₂O.

range of temperature there are two concentrations at which the solution is saturated with respect to HBr.2H₂O, one containing more and the other less HBr than the substance crystallising out.

The curve AFB represents a three-phase system of two components with one degree of freedom. If one condition of the system is altered, keeping the others constant, one of the phases must disappear. For example, if it is cooled under constant pressure, it moves off the curve AFB to the left, the solution freezes to dihydrate, which then exists in the presence of vapour only, so that in the area AFBC only a bivariant system remains. If now the pressure, that is the concentration of HBr, is raised, the monohydrate, which is poorer in water than the dihydrate, is formed. On the section CB, dihydrate, monohydrate and vapour are in equilibrium without any liquid phase. This curve cuts the curve FB, which gives the limit of existence of the solution, at the point B, which is a quadruple point, since a fourth phase, the solution, is added to the three already in existence along CB. The system is now nonvariant, with four phases and two components. If the pressure or the temperature is increased one of the phases (dihydrate) disappears, and the three left form a univariant system existing along the curve BL. The concentration of HBr increases continuously and is everywhere higher than that required to form dihydrate. If the concentration is further increased, liquid HBr appears as well as the monohydrate, so that a new quadruple point is reached at L, where monohydrate, liquid HBr, solution and vapour coexist. A further increase in HBr concentration causes yet another component, the monohydrate, to disappear, so that in the final portion of the curve LE only liquid HBr, solution and vapour are in equilibrium. This portion of the curve is naturally only obtainable under considerable pressure. This is often the case when the formation of hydrates which contain but little H₂O is being investigated, and if they are looked for only at atmospheric pressure they may easily be missed. The point B is, however, obtained at a pressure of less than one atmosphere.

Finally, we must consider the curves BZ and LX. If we imagine the system at the quadruple point B in a closed apparatus in which it can be compressed without introducing any fresh hydrogen bromide, then the gas phase will soon disappear owing to compression. Only monohydrate, dihydrate and solution will then coexist; and if compression is continued the component with the greatest volume will disappear. For, according to Le Chatelier's principle, the pressure will tend to be equalised by the system assuming the smallest possible volume, and at a transition point the densest phase will be formed. In this instance the hydrates are denser than the solution, so that pressure converts solution into solid hydrates, and even favours their formation so much that they exist at temperatures above B—the higher the pressure the higher the transformation temperature. The curve BZ is practically vertical but actually slopes slightly to the right. The curve LX is similar; here the three phases, monohydrate, solution, and liquid HBr, exist in univariant equilibrium. If the pressure is increased the dense monohydrate tends to be formed, and thus this compound exists under pressure at temperatures as high as L.

At low temperatures a tri- and tetrahydrate exist in this system.

To determine these hydrates it is not enough to determine the composition of the solid phase settling out; for besides the substances characterised as compounds by the laws of simple and multiple proportions, substances of constant composition may separate out in which the proportions are not simple. These are eutectic mixtures.

HALOGEN SALTS—GENERAL—UNIVALENT METALS

General behaviour—Alkali halides—Halides of the univalent heavy metals

General Methods of Formation

THE halogen salts are formed synthetically from their elements (*e.g.* M + Cl $\longrightarrow$ MCl) by decomposition of the acid or metallic oxide (*e.g.* M + HCl $\longrightarrow$ MCl + H or MO + Cl $\longrightarrow$ MCl + O, etc.) or by decomposition of more complex compounds (*e.g.* MClO₃ $\longrightarrow$ MCl + 3O).

Synthesis.—The following table gives the heat of formation of some halogen salts:

	F	Cl	Br	I
K	118·1	105·6	95·3	80·1 Cal.
Na	102·6	97·7	85·7	69·0 ,,
½Ba	111·3	98·4	86·0	68·0 ,,
½Ca	106·8	91·9	77·5	74·5 ,,
Ag	23·2	29·4	22·7	13·8 ,,

In general this value decreases in passing from fluoride to iodide, but the silver salts form an exception to this rule, as the fluoride is both less exothermic and more soluble than the chloride. The heat of formation of AgCl includes an unknown heat of polymerisation. When the heat of formation of salts of the same halogen with different metals is compared, the order is approximately that of the electromotive series (p. 151) and the most electropositive metals have the highest heat of formation of halide. But the parallel is not exact in detail: even in the short table given above it is seen, for example, that the heat of formation of barium iodide is less than that of calcium iodide, and in a more comprehensive list the exceptions would be much more numerous. Similar discrepancies occur in the formation of oxides and of sulphides (p. 441).

The preparation of halides by direct synthesis from metal and halogen is often difficult owing to the formation of a layer of halide on the surface of the metal, which prevents further action. Hence even fluorine can be kept in vessels of various metals, *e.g.* copper. The alkali and alkaline earth metals combine completely with fluorine, but magnesium, aluminium and zinc resist its action at ordinary temperatures, as they

become coated with a thin layer of fluoride. On warming more or less vigorously, however, all metals are attacked; also, if the metals are finely divided, the heat developed by the reaction at the surface causes the action to go on to completion, not only in fluorine but also in chlorine and even in bromine. Finely powdered metals take fire when sifted into chlorine or bromine provided the gases are not quite dry. With thoroughly dried halogens, even the alkali metals do not react and can be kept in them for years with untarnished surfaces. The noble metals react with chlorine when in the form of fine powder, though they do not catch fire.

If the layer of halide is continuously removed from the surface of the metal, the reaction goes to completion even with large pieces of metal. The presence of water, when the halide is soluble, easily effects this, and iodides, for example, can be made from iodine and metal in the presence of water; this is the usual method of preparing many iodides (e.g. that of iron).

Decomposition Methods.—The formation of halides on decomposition of oxy-halogen compounds, such as hypochlorites, hypobromites, chlorates, perchlorates, periodates, etc., will be mentioned when those compounds are considered.

Decomposition of other Metallic Compounds.—The preparation of halides by treating some other compound of the metal with free halogen is useful, but seldom employed. The preparation of halides from oxides and from sulphides is usually difficult, although silver oxide is easily transformed. Aluminium oxide, for example, only begins to react with chlorine at a white heat; but if finely powdered carbon is mixed with the oxide the reaction proceeds at a lower temperature. A convenient method is to mix the oxide with some oil, make the mass into balls, and carbonize in absence of air. The production of chloride then takes place at a low red heat. Carbon tetrachloride is first formed and reduces the oxide by virtue of the carbon it contains, and the joint reaction increases the total thermal effect, so that the desired reaction proceeds at a lower temperature. The vapour of carbon tetrachloride may also be used direct by passing it over the red-hot oxide; this method is particularly applicable to the preparation of the chlorides from oxides difficult to reduce, such as those of aluminium, thorium and chromium. Sulphur monochloride, S_2Cl_2, can also be used [1] when the sulphur acts as reducing agent and sulphur dioxide is formed together with the chloride.

The halogen acids and other halogen compounds can be used in place of the free elements, and halides are formed when metals, oxides, hydroxides, carbonates, etc., are dissolved in the acids. Only the more electropositive of the free metals are soluble, but some of the others dissolve in the presence of oxygen. Even gold and platinum

[1] Matignon and Bourion, *Compt. rend.*, 1904, 138, 631, 760.

are soluble to a considerable extent in warm concentrated hydrochloric acid when oxygen is present. Possibly the metal acts as a catalyst to the reaction $2HCl + O \longrightarrow H_2O + Cl_2$ (the Deacon process, p. 166), and is then attacked by the liberated halogen.

For the preparation of anhydrous fluorides, metallic fluorides can be used in place of free HF. The metal of which the fluoride is required is heated with the other fluoride thus: $PbF_2 + M \longrightarrow Pb + MF_2$. The fluorides of lead and mercury are used, as they are volatile when heated; Ruff and Graf[1] have used gaseous arsenic pentafluoride as a direct fluorinating agent, while antimony trifluoride, with SbF_5 as catalyst, has proved an effective fluorinating agent in the preparation of fluorides and chlorofluorides of Si, Se, etc.

Halides which are fairly insoluble, e.g. AgCl, can be obtained from aqueous solutions by double decomposition.

General Properties

All metallic halides are solids, while halogen compounds of the non-metals are mostly liquid or gaseous. Metals which are nearly related to the non-metals, or which can combine with many halogen atoms, also form liquid halides; but these do not behave as salts. Thus tin tetrachloride, arsenic trichloride and antimony pentachloride are liquids. Arsenic pentafluoride is gaseous, as are also the non-metallic halides SiF_4, PF_3, PF_5 and BF_3. Another difference between the halides of the metals and those of the non-metals lies in the variation in volatility with increasing proportion of halogen. In the metallic compounds the volatility increases as we pass from fluoride to iodide, while with non-metals it decreases with increasing atomic weight of the halogen; that is, the iodide is the most volatile of metallic halides, the least volatile of non-metallic halides. This may be connected with the fact that the crystals of the halides of metals of low valency have ionic lattices, and their cohesion is increased by the alternation of metal and halogen ions of opposite polarity. Compounds which are rich in halogen, on the other hand, such as the easily liquefied and vaporised compounds of the non-metals, have the typical covalent structure. In the first case the sequence in the lattice is $X-M-X-M-X-M-$, in the second $X-M-X \cdot X-M-X \cdot X-M-X$, and in the latter, since two halogen atoms are always next to each other, separation is more easily effected in the absence of the electric attraction. Compounds of the second type, therefore, have low melting points and low boiling points. In consequence, also, the less easily fusible halides are good conductors of electricity when they are fused, while those easily melted are poor conductors, since in the former the ions are already present in the crystal.[2]

The crystallographic form of the crystal is also dependent to a marked degree on the electrical forces between the atoms (cf. p. 829). According to Goldschmidt's

[1] Ber., 1906, 39, 67.   [2] Kossel, Z. Elektrochem., 1920, 26, 314.

fundamental law of crystallography[1] the structure of a crystal is dependent on the relative masses, the relative sizes and the polarisation properties of its components. Under the last heading is included the tendency to deformation due to the electrical fields of neighbouring atoms (*cf.* pp. 35, 39) and also the distortion produced by the action of the crystal units on the other atoms. The polarising action increases similarly to the tendency to deformation and varies directly with increase in the ionic charge and inversely as the ionic radius, when the charge on the ion is the same. The following table gives the polarisability of the more important types of ions ; but the numbers are only comparable for ions of the same structure :

Univalent positive ions		Li	Na	K	Rb	Cs
		1.7	1.0	0.6	0.5	0.4
Bivalent positive ions		Be	Mg	Ca	Sr	Ba
		4.0	3.3	1.8	1.2	1.0
Tervalent positive ions		Al	Sc	Y	La	
		9.2	4.4	2.7	2.0	
Quadrivalent positive ions		Si	Ti	Zr	Ce	Th
		26.0	9.8	5.3	3.8	3.3
Univalent negative ions		F	Cl	Br	I	
		0.6	0.3	0.3	0.2	
Bivalent negative ions		O	S	Se	Te	
		1.1	0.7	0.5	0.5	

The effect is most marked when a strongly polarising ion such as sexavalent sulphur (+ve) and a strongly polarisable ion such as bivalent oxygen (−ve) are joined together as in the formation of the SO_4'' group. Such groups frequently appear in crystals as inseparable units and are the familiar radicals of chemistry. The polarising action of the sulphur atom on the oxygen atom is contra-polarised by the metal present ; for instance, in $CaSO_4$ both the calcium and the sulphur atoms attract the oxygen atom, in a sense competing with each other. In ammonium fluoride, NH_4F, the contra-polarisation of the fluorine by the hydrogen is so great that one of the H atoms, as may be seen by the X-radiogram, is strongly pulled towards the F atom. The ionic compound $NH_4{}^\cdot F'$ is distorted towards the non-polar $NH_3 + HF$, and so the substance is volatile at a low temperature and breaks down into NH_3 and HF.

Chlorides are usually more volatile than the free metal. The volatility increases with increasing valency of the metal—that is, with increasing halogen content—so that the halides of tervalent metals such as aluminium and iron can be sublimed at a red heat and thus freed from impurities. But there is always a risk that the halides of multivalent metals will dissociate before sublimation, with liberation of free halogen. Thus, although aluminium chloride can be sublimed easily, ferric chloride is converted into ferrous chloride, cupric chloride into cuprous chloride; H_2PtCl_6 or H_2PtBr_6 form first $PtCl_4$ and $PtBr_4$, and finally $PtCl_2$ and $PtBr_2$. This decomposition can sometimes be avoided by subliming in an atmosphere of the halogen (*e.g.* with $FeCl_3$), but only when the dissociation pressure of the halogen at the temperature of sublimation does not exceed one atmosphere. In other compounds, *e.g.* $CuCl_2$, $PtCl_4$ and $AuCl_3$, the pressure required is so high that the chlorides can be sublimed only under increased pressure. These compounds thus break up on heating into lower oxidation products and free halogen before sublimation.

[1] V. M. Goldschmidt, *Geochemische Verteilungsgesetze*, Oslo, VIII., 1926.

The decomposition of the chlorides of those metals which form a long range of chlorides is particularly interesting. L. Wöhler and S. Streicher[1] have studied the series:

$$IrCl_4 \text{------} IrCl_3 \text{------} IrCl_2 \text{------} IrCl \text{------} Ir$$

and

$$PtCl_4 \text{------} PtCl_3 \text{------} PtCl_2 \text{------} PtCl \text{------} Pt.$$
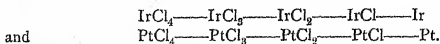
The range of existence of these compounds at atmospheric pressure is indicated in the following diagram. The compound $IrCl_4$, which has a dissociation pressure of five atmospheres at room temperature, is not shown.
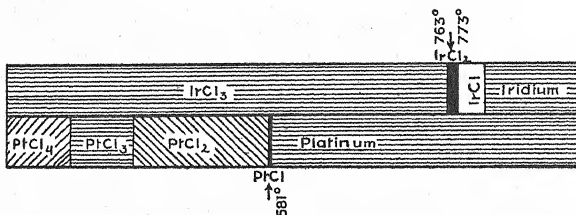
FIG. 32.—Stability of the chlorides of iridium and platinum.

The temperature ranges in which these compounds exist is seen to be quite irregular: that of $IrCl_3$ is large, of $IrCl_2$ very small, of $IrCl$ a little larger. Of the platinum compounds, again, $PtCl_3$ has a small range, though not so small as that of $PtCl$. $RhCl$ is obtained by heating $RhCl_3$ above 900°; $RhCl_2$ is formed simultaneously. There is no evidence concerning the molecular complexity of these lower halides.

Solubility and Solutions.—Chlorides and bromides are soluble in water except those of the univalent heavy metals, Ag, Cu, Tl, Hg and Au, the chloride of bivalent lead (soluble to some extent in hot water) and of platinum, and palladium bromide. The insolubility of the univalent chlorides is best considered in the light of the position of the elements in the periodic system. The halides of multivalent metals regularly form hydrates, and it is these hydrates which dissolve in water; the anhydrous halides are sometimes insoluble. Thus anhydrous chromium chloride, $CrCl_3$, may remain in contact with water for a long time undissolved, and only on the addition of a catalyst (*e.g.* a little of a chromous salt) does it dissolve, becoming hydrated at the same time.

The iodides of metals which have insoluble chlorides are also insoluble. The iodides of a few metals of higher valency are insoluble, differing in this way from their chlorides and bromides: BiI_3, AuI_3, HgI_2, and PdI_2 are precipitated from aqueous solution, probably because they form no hydrates.

[1] *Ber.*, 1913, 46, 1591.

The fluorides are in general the least soluble of the halides. Those of the alkaline earths, of Mg, Al, Zr, and even of Pb and Cu, are insoluble. Others are but slightly soluble, e.g. the fluorides of bivalent chromium, mercury and manganese. The fluorides of Ag, Hg, and Tl are quite readily soluble, and the sequence of decreasing solubility is F $\longrightarrow$ Cl $\longrightarrow$ Br $\longrightarrow$ I.

Some negative radicals are very similar to the halogens in the formation of salts. The cyanide radical, $-CN$, the thiocyanate radical, $-CNS$, and that of hydrazoic acid, $-N_3$, are among these "pseudo-halogens." They give precipitates with the same metallic ions as the chloride ion, and the solids thus formed are very similar in appearance to the chlorides. Salts of these radicals have the same crystalline form as the chlorides and the same tendency to form complex compounds. They will be considered with the various halides.

The aqueous solutions of the halides of the alkalis and of the alkaline earths are neutral in reaction (fluorides of the alkali metals react alkaline), but the halides of most of the heavy metals are acid in solution owing to hydrolysis. The action of water is as follows:

$$MCl + HOH \rightleftharpoons M(OH) + HCl.$$
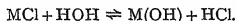
The hydroxide is a weak base, while the halogen acid is a strong acid; hence there are more H˙ ions than OH′ ions in solution, and the liquid therefore has an acid reaction. As a rule, the equilibrium is well on the left side of the equation, and not enough hydroxide is formed to cause precipitation. With salts of bismuth and antimony, however, the reaction proceeds so far towards the right that the solubility product of the hydroxide, or of an intermediate basic salt, is exceeded and precipitation occurs. In order to preserve equilibrium more must be formed in the solution, and these changes go on until the concentration of HCl is sufficient to prevent further decomposition of the chloride of which the concentration is now reduced. The deposition of the hydroxide can be prevented altogether by the addition of excess of hydrochloric acid. Such an excess has a different effect when the solubility product of the chloride itself is low. This is soon exceeded when the acid is added and the chloride itself is precipitated. The effect occurs easily with NaCl, $BaCl_2 . 2H_2O$, and even with $AlCl_3 . 6H_2O$. This phenomenon is used for the purification of suitable chlorides by saturating their solutions with hydrochloric acid, when they crystallise out and leave the more soluble chlorides in solution.

The halogen acids react in another way with other halides. The halides of Cu˙, Ag, Pb and Hg˙˙ are more easily soluble in excess of acid than in water, as they form addition compounds with formulae approximating to $[AgCl_2]H$ and $[CuCl_2]H$. The halides of Sn˙˙ are precipitated from solution on the addition of a small quantity of acid, but redissolve in more concentrated acid—they are salted out in dilute

solution, but form addition products in the stronger acid. Complex acids are similarly formed by many organic bases. All the halogen acids form these compounds; those of hydrofluoric acid, which is itself polymolecular in the free state, are easily isolated. With potassium the following compounds are formed: KF, KHF_2, KH_2F_3, KH_3F_4, and similar rubidium and silver salts exist. The following compounds of hydrochloric acid can be prepared in the solid form:

$CuCl$, HCl	$ZnCl_2$, HCl, $2H_2O$	$AuCl_3$, HCl, $4H_2O$	$PtCl_2$, HCl, $2H_2O$
$CuCl_2$, HCl, $3H_2O$	$SnCl_2$, HCl, $2H_2O$	$BiCl_3$, HCl, $3H_2O$	$PtCl_4$, HCl
$CuCl_2$, $2HCl$, $5H_2O$	$HgCl_2$, HCl	$SnCl_4$, $2HCl$, $6H_2O$	$PtCl_4$, $2HCl$, $6H_2O$
$CuCl_2$, $3HCl$	$CdCl_2$, $2HCl$, $7H_2O$	$SbCl_3$, HCl, $1, 2 \& 3H_2O$	etc.

and hydrobromic and hydriodic acids give similar compounds. All these compounds are complex acids, and are analogous to the double halides which are discussed later (p. 265, etc.).

✓✓ The metallic halides and cyanides are considerably dissociated in solution, with the remarkable exception of those of bivalent mercury; the cyanide in particular scarcely gives the reactions of the $Hg^{..}$ ion at all. Cadmium halides are also very feebly ionised, especially the iodide. In non-aqueous solutions the ionisation of some iodides is high; potassium iodide dissolves considerably in the most varied solvents, and the solutions frequently conduct the electric current.

✓✓ Halogen compounds conduct the electric current in the fused condition to an extent which depends in some measure on whether the halogen atoms enclose the central atom or no. In the enclosed compounds there is no oppositely charged ion in apposition, and the central atom is screened off from the field of force. The following table

EQUIVALENT CONDUCTIVITY AT THE MELTING POINT

HCl 10^{-6}			
$LiCl$ 166	$BeCl_2$ 0·086	BCl_3 0	CCl_4 0
$NaCl$ 133·5	$MgCl_2$ 28·8	$AlCl_3$ $1·5 \times 10^{-5}$	$SiCl_4$ 0
KCl 103·5	$CaCl_2$ 51·9	$ScCl_3$ 15	$TiCl_4$ 0
$RbCl$ 78·2	$SrCl_2$ 55·7	YCl_3 9·5	$ZrCl_4$?
$CsCl$ 66·7	$BaCl_2$ 64·6	$LaCl_3$ 29·0	$HfCl_4$?
...	...	...	$ThCl_4$ 16

shows that the increase in ionic volume of the central atom (tabulated from the top right) must reach a certain value before it can be considered as enclosed.[1] There is thus a sharp division into polar and non-polar substances, the separation being shown in the table by the heavier lines; ionisation is promoted by the small charge and large size of the cation (Fajans).

Many water-soluble halides can be obtained in the colloidal condition in non-aqueous media and even in alcohol-water mixtures.[2]

Colour.—The halogen ions are colourless, and colour in the salts is usually due to the metals.

The iodides are often exceptions to this rule, particularly those which are anhydrous and insoluble in water. A yellow colour is common; AgI and CuI are pale yellow, TlI and PbI_2 are bright yellow, HgI and AuI_3 greenish yellow, BiI_3 and PdI_2 dark brown, SnI_2 orange, and HgI_2 a brilliant red. Even hydrated salts, which have a colour due to the metal ion, assume a different one when dehydrated. Thus anhydrous cupric chloride is yellow, cupric bromide is black, the thiocyanate is velvet black; the chloride and bromide of nickel are yellow, and its iodide is black; anhydrous cobalt chloride is pale blue, the bromide brilliant green, the iodide black like graphite. The different hydrates of the same salt have different colours. The colour of the ions is often entirely different from that of the undissociated substance, not only in halides but also in other salts; but if the salts contain water the colour approximates to that of the ion, for on dissociation in water hydrates are formed of the radicals capable of combining with water. The following table illustrates the variation in colour:

Mol. H_2O.	0	1	2	6	9
$NiCl_2$ . .	Golden yellow	Yellow green	Green	...	...
$CoCl_2$ . .	Blue	Violet	Rose-red	Red	...
CoI_2 . .	Black	...	Green	Red	Bright red

On the other hand, the manganese salts are all pale rose-red throughout the range of o—9 mols. of water of crystallisation, except the thiocyanate, which is yellow when anhydrous, green when hydrated, and red in solution.

Structure of the Crystal Lattice.—There are in general three ways in which the atoms of metal and halogen can be arranged in halide crystals. They may be packed in such a way that the ordinary molecular formula is reproduced in the crystal, each molecule being

[1] Biltz and Klemm, *Z. anorg. Chem.*, 1926, 152, 267.
[2] P. P. v. Weimarn, *Kolloid Z.*, 1913, 12, 303, and *Die Allgemeinheit des Kolloid-zustandes*, Dresden, 1925.

separated from the others. This is a *molecular lattice* and is formed when the halogen and metal atoms, as a consequence of strong polarisation, are drawn close together, or when there are enough halogen atoms to surround the metal atom completely, so that it is unable to influence the atoms of adjacent molecules. An example of this is seen in SnI_4, in which each molecule forms a separate design in the crystal.

The second arrangement is seen when positive and negative ions are arranged equidistant from one another in all six directions at right angles. An example of this is to be observed in the sodium chloride lattice (Fig. 46, p. 299). Here a metal ion is not connected with a single halogen ion but is co-ordinated with six, and similarly each halogen ion is equally related to six metal ions. A lattice of this type is called a *co-ordination lattice*. There are many types of arrangement in this class; but it differs from the molecular lattice in the dominant influence of the size of the ions, as the effect of polarisation is small owing to the equal influence on any unit from all sides.

Between the extreme types of co-ordination and molecular lattice is the *layer lattice*, which in two dimensions can be regarded as a co-ordination lattice but in the third has the features of a molecular lattice. It is formed when the polarising action is moderate, and cadmium iodide is a good example of this type. (Fig. 89, p. 886). In these crystals the cadmium atoms lie in a plane and above and below are planes containing iodine atoms; so that when the three planes are placed above one another the sequence of atoms is $I-Cd-I$ $-I-Cd-I-I-Cd$, etc. The iodine atoms which come next one another have very little effect on one another owing to the charge being of the same sign. Hence the layers of thickness $I-Cd-I$ easily separate and crystals of this type are usually leaflets, readily split along one plane. They are also more readily volatile than substances forming co-ordination lattices. These three types of packing are not confined to the halides but are quite general, and oxides, sulphides, nitrides, etc., all conform to these general rules.

Halides of the Alkali Metals

Production.—Sodium and potassium chloride occur naturally in such large quantities that only a process of purification is necessary to supply the quantities used in commerce. A simple crystallisation is sufficient for sodium chloride, but as potassium chloride exists only in moderate quantities as sylvine, KCl, and mostly in double salts, it must first be separated from the other constituents. These double salts are obtained from the "Abraumsalze" (so called, because they were originally rejected as useless). They occur in particular at Stassfurt,

lying above the deposits of rock salt. When a limb of the ocean was cut off and dried up, the less soluble sodium chloride separated first, and the mother liquor containing the more soluble calcium, potassium and magnesium salts dried up later. The calcium sulphate, being less soluble in warm solution, separated mostly in summer, while the other salts, being less soluble in cold water, crystallised out in winter. Thus the course of evaporation can be followed by observing the annual rings. A waterproof layer of clay was deposited on top by the action of quicksands. When this is penetrated, the valuable potassium salts, originally cleared away to expose the rock salt below, are reached.

The "Abraumsalze" (see also pp. 260, 261) are chiefly made up of:

Carnallite .	.	.	$KCl, MgCl_2, 6H_2O$	ca. 55-65	per cent.
Kainite	.	.	$KCl, MgSO_4, 3H_2O$	,, 1-2	,,
Kieserite .	.	.	$MgSO_4, H_2O$	,, 10-20	,,
Tachhydrite	.	.	$2MgCl_2, CaCl_2, 12H_2O$	,, 2-4	,,
Rock salt .	.	.	$NaCl$	,, 20-25	,,

Carnallite, and to a lesser extent kainite, is used as the source of potassium chloride. The carnallite is first freed from foreign matter and then decomposed into its components. It is more soluble than the rock salt and kieserite which accompany it but it cannot be purified by recrystallisation as it is decomposed by water and separates out only when a considerable excess of magnesium chloride is present. A concentrated solution of magnesium chloride, such as is obtained in the subsequent decomposition of the carnallite, is therefore used to recrystallise the raw salt. This when hot does not dissolve the kieserite or the clay, and by fractional crystallisation gives pure carnallite. The mother liquor contains the bromine salts (brom-carnallite) as well as the rubidium and caesium salts. If carnallite is treated with water, potassium chloride crystallises and magnesium chloride remains in solution; but this recrystallisation method can be avoided by applying the discovery of Meyerhoffer, that carnallite melts in its water of crystallisation and is decomposed into its components above 167°; potassium chloride separates out, and a solution containing the whole of the magnesium chloride and a small quantity of potassium chloride can be removed. The hot extraction gives a purer potassium chloride, but costs more.

Rubidium and caesium chlorides were formerly made by prolonged recrystallisation of carnallite, which contains these metals as alums. The caesium alum is the less soluble. A much better way of obtaining these rare alkalis, however, is by precipitation with silicomolybdic acid; the caesium is in the first precipitate. The precipitated salt is then treated with gaseous HCl, to volatilise molybdenum, and the remaining chlorides are fractionally crystallised from alcohol. Caesium

is finally isolated as the sparingly soluble double salt with antimony trichloride.[1]

The alkali bromides and iodides do not occur in compact masses in nature, and are made in practice from the free halogen and the alkali hydroxide. This method, however, gives mixtures of bromide and bromate, or of iodide and iodate: $3I_2 + 6KOH \longrightarrow 5KI + KIO_3 + 3H_2O$. The mixture is therefore evaporated and the iodate reduced, e.g. by heating, or with carbon, or by a stream of sulphuretted hydrogen. The iodate from Chile saltpetre is usually reduced with bisulphite.

Another method is available for making iodides. If iodine itself is rubbed with iron filings, Fe_3I_8 is formed and can be decomposed with alkali carbonate, thus:

$$3Fe + 4I_2 \longrightarrow Fe_3I_8; \quad Fe_3I_8 + 4K_2CO_3 \longrightarrow 8KI + Fe_3O_4 + 4CO_2.$$
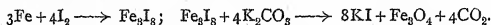
Properties.—All the anhydrous alkali halides crystallise in cubes. When foreign salts are added to the solution, the habit is different, although the crystal system is not altered. Thus potassium chloride crystallises in octahedra in the presence of potassium carbonate, while mercuric chloride causes the formation of rhombododecahedra, and hydrocarbons that of icositetrahedra. Common salt also crystallises in octahedra from solutions containing urea. When these compounds crystallise, drops of the mother liquor are enclosed, which vaporise with production of considerable pressure when the crystals are heated, so that the crystal is broken up and the fragments flung about (decrepitation). The "knistersalze" of Wieliczka owe their peculiar property to the same phenomenon, for hydrocarbons are enclosed under pressure in the rock salt, and when it is put into water they burst it with a low crackling noise.

Some natural rock salt is blue in colour. The colour is due, not to a subchloride or foreign colouring matter as was previously supposed, but to free sodium contained in the crystals in a finely divided form. The quantity dissolved in the blue rock salt is so minute that it cannot be detected when the salt is dissolved in water, but it can be detected by the ultramicroscope. Blue rock salt can be made artificially, either by heating sodium chloride in sodium vapour or by exposing the salt to cathode rays or to radium. The colour is lost on ignition as the sodium distils. The blue salt in nature is probably due to radioactive processes, and this theory of its origin is confirmed by the presence of helium and neon in the salt beds, sometimes in considerable quantities. It is possible that potassium is the cause of the phenomenon, as it is somewhat radioactive (p. 84); but if so, it is strange that the blue rock salt is not more regularly contaminated with potassium salts. A blue sylvine is also found.

Changes in colour as a result of irradiation also occur in many other substances. Thus sapphire becomes yellow when exposed to radium, but shows its original colour when viewed with an arc-lamp. According to Doelter,[1] fluorspar, celestine, zircon, topaz, rutile and other coloured minerals owe their colour, or part of it, to radioactive action. Artificial stones can be distinguished from natural stones by the different colour change when exposed to radium.
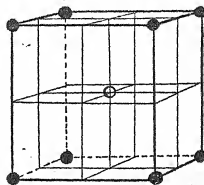
Crystal Structure.—All the halides of Li, Na, K, Rb, and also caesium fluoride, have a face-centred cubic lattice of the type figured in Fig. 46 (p. 299), the atoms of metal and halogen alternating with one another. In the three other caesium halides, however, the structure is a body-centred cubic lattice,

FIG. 33.—CsCl Lattice.

with a caesium atom at each of the eight corners of the cube and halogen atoms at the centres of the cubes (Fig. 33). The ammonium halides are similar to these halides of caesium, but their structures are dependent on temperature, the transition points being: NH_4Cl, 184.3°; NH_4Br, 137.8°; NH_4I, −14.6°. Above these temperatures they have the usual rock salt structure. The cause of the difference in crystal structure between Cs halides and the others is the large volume of the Cs˙ ion round which eight Cl′ ions can be grouped, while the smaller Na˙, etc., can accommodate only six.

The sides of the unit cubes are as follows:

	Li	Na	K	Rb	Cs	NH_4	
F .	4·01	4·62	5·33	5·66	6·01	...	...	Å.
Cl .	5·13	5·63	6·28	6·53	*4·12*	6·53	*(3·86)*
Br .	5·49	5·94	6·57	6·84	*4·29*	6·90	*(3·99)*
I .	6·06	6·46	7·05	7·31	*4·56*	7·20	...

The figures in *italic* refer to the body-centred types.

Solubility.—The alkali halides, except those of lithium, are not hygroscopic, showing that their saturated solutions have a higher vapour pressure than the usual pressure of water vapour in the atmosphere. Impure common salt becomes damp on exposure to the air, because the magnesium chloride which it contains is hygroscopic.

The solubility of the more important alkali halides in water is shown by the curves in Fig. 34; the solubility increases from chloride to iodide except in the case of caesium. The small temperature coefficient of the solubility of sodium chloride is remarkable, and makes it easy to separate common salt from mixtures by fractional

[1] *Monatsh.*, 1911, 32, 299.

crystallisation. Most other salts are much more soluble in hot than in cold water, and consequently crystallise out when a hot saturated solution is cooled, while only a little of the sodium chloride is deposited. This fact is applied in the purification of saltpetre and in the manufacture of nitre from saltpetre.

In non-aqueous solvents also the solubility increases from chloride to iodide. Potassium iodide in particular is soluble in many inorganic and organic liquids, and these solutions are often electrolytes. It dissolves readily in liquid ammonia and liquid sulphur dioxide, probably with formation of compounds analogous to the salt hydrates. Its solubility in absolute alcohol, however, is low (2·5 per cent.
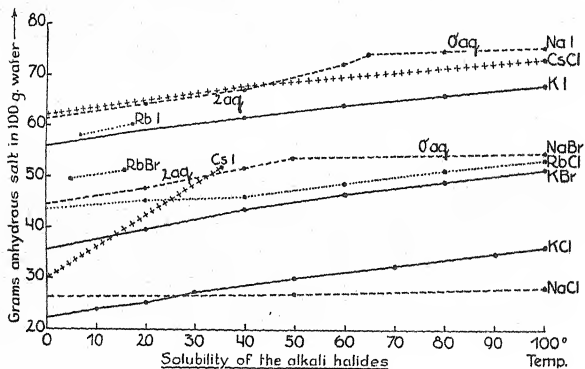
FIG. 34.

at room temperature), but not so low as that of the chloride (0·034 per cent.); the solubility of both increases considerably on addition of water to the alcohol.

Melting and Boiling Points. — The following table gives the melting points of the alkali halides :

	F	Cl	Br	I
Li .	842°	606°	549°	446°
Na .	988°	800°	740°	660°
K .	846°	768°	728°	693°
Rb .	775°	713°	681°	642°
Cs .	684°	626°	627°	621°

For a given metal the melting point falls with increase in the atomic weight of the halogen. In the series Na—K—Rb—Cs the decrease is

the greater the higher the melting point of the fluoride; for instance, the difference between chloride and iodide is:

Na	K	Rb	Cs
140°	75°	71°	5°

These halides volatilise at high temperatures without decomposition. At 2000° the vapours are composed of simple molecules.

The boiling points of the alkali halides at 760 mm. are[1]:

	Li	Na	K	Rb	Cs
F .	1676°	1695°	1505°	1410°	1251°
Cl .	1382°	1441°	1417°	1383°	1303°
Br .	1310°	1393°	1381°	1351°	1300°
I .	1170°	1300°	1331°	1305°	1280°

The boiling points drop steadily from fluoride to iodide. In the series of the metals they are lower at the two ends and reach a maximum in the sodium salts; potassium iodide is the only one in which the boiling point (as also the melting point) is higher than that of the sodium salt. The boiling points of the fluorides lie wide apart; but with rising atomic weight of the halogen the b.p. of the halides approach nearer together.

Volume Relations.—The following table displays the volume relations of the alkali halides. The molecular volume is the number of c.c. occupied by a gram molecule.

	LiF	LiCl	LiBr	LiI	NaF	NaCl	NaBr	NaI
Sp. gr. .	2·29	2·07	3·46	4·06	2·77	2·18	3·20	3·66
Mol. vol. .	11·30	20·50	25·08	32·96	15·18	26·98	32·13	40·91

	KF	KCl	KBr	KI		RbCl	RbBr	RbI
Sp. gr. .	2·48	1·99	2·75	3·12	...	2·80	3·35	3·43
Mol. vol. .	23·42	37·49	43·30	53·30	...	43·21	49·38	61·95

	CsCl	CsBr	CsI
Sp. gr. .	3·97	4·43	4·51
Mol. vol. .	42·34	47·99	57·62

These numbers give interesting data for investigating the alteration in volume when a compound is formed, as the molecular volumes of the free elements are known.[2]

Richards[3] detected a relation between the volumes of the components and that of the compound formed from them. The contraction increases as the heat of formation increases, as shown in Fig. 35. He therefore regards the heat of reaction as in essence a heat of compression. The two curves in the diagram show the parallelism

[1] v. Wartenberg and Schulz, *Z. Elektrochem.*, 1921, **27**, 568.
[2] *Cf.* Ephraim and Michel, *Helv. Chim. Acta*, 1919, **2**, 266; 1924, **7**, 298.
[3] *Z. physikal. Chem.*, 1902, **40**, 169, 597; 1903, **42**, 129.

between heat of formation and heat of compression of the common bromides.

General Properties.—The halides of lithium, and to a lesser extent those of sodium, differ from those of the general series — potassium, rubidium and caesium. The lithium salts are more like those of the alkaline earths; thus the fluoride is not very soluble in water and lithium halides easily form complex compounds with ammonia, amines, alcohols and ketones, a property which the other alkali halides lack. They also contain water of crystallisation at ordinary temperatures and retain part of it tenaciously at temperatures above 100°, while the other alkali halides are usually anhydrous. Some of the sodium salts also contain water of crystallisation at low temperatures, while the other alkali halides are known only in the anhydrous condition. The difference in the water content of sodium and potassium compounds also appears in salts other than halides; *e.g.*:
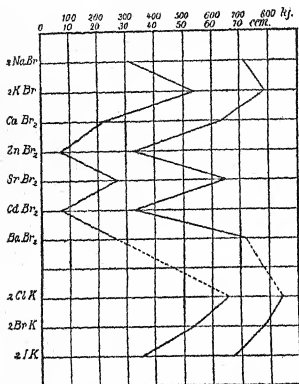
FIG. 35.—Contraction and heat of formation.

Na_2SO_4, $10H_2O$ Na_2CO_3, $10H_2O$ Na_2HPO_4, $12H_2O$
K_2SO_4 anhydrous K_2CO_3 anhydrous K_2HPO_4 anhydrous
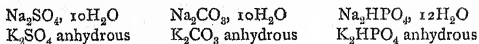
Similarly, the crystal form and the solubility of the sodium salts is often different from that of the K—Rb—Cs salts. Thus the K—Rb—Cs salts of chloroplatinic acid and perchloric acid are practically insoluble, the sulphate, tartrate and cobaltinitrite only slightly soluble, but the corresponding sodium salts are easily soluble and even deliquescent. In other examples the potassium salt is deliquescent and the sodium salt is well crystallised.

The ammonium halides, which are like those of the alkali metals in many ways, are more akin to those of potassium than to those of sodium. The reason for this is that the ionic volume of the ammonium is closer to that of potassium than to that of sodium. In many properties the ammonium salts lie between potassium and rubidium, particularly in solubility. In fact the members of the series NH_4—K—Rb—Cs show less variation in their properties and in those of their compounds than the members of any other group except possibly the halogens.

Polyhalides.—Iodine is much more soluble in solutions of potassium iodide than in water. When a solution of iodine in potassium iodide is evaporated large black crystals are obtained, which have a formula approximating to KI_3. This compound is extremely soluble. In passing from K to Rb and Cs the iodine addition compounds become less soluble and more stable. Thus caesium polyiodides are fairly insoluble and very stable. The ammonium compounds are similar to those of potassium.

The quantity of iodine which dissolves in aqueous solution increases with increasing concentration of the alkali halide. It must not, however, be assumed that compounds with higher iodine content are formed; for the polyiodides contain such a high percentage of iodine that they tend to behave somewhat similarly to the element itself. Substances which are chemically similar always tend to form mixtures, such as solid solutions or mixed crystals, or to increase the solubility of each other in a given solvent. In a concentrated solution of potassium iodide quantities of iodine up to eight or more atoms per molecule can be dissolved, and still larger quantities of iodine can be dissolved by melting KI_3 with iodine; but it is very improbable that these are compounds. When these solutions are diluted the iodine which is present in excess of the tri-iodide formula is precipitated. The following polyiodides are definite in crystal form and properties:

$$KI_3 \text{ (decomp. at } 25°), \quad NH_4I_3, \quad RbI_3, \quad CsI_3, \quad CsI_4.$$

The hydrates KI_3, H_2O; KI_3, $2H_2O$; KI_7, H_2O; Na_4I_{14}, $13 \cdot 15$ H_2O; Na_5I_{11}, 17-19 H_2O; and Na_2I_8, 10-11 H_2O are also known.

Recently the polyiodides of ammonium, sodium, potassium and rubidium have been further studied[1] and several new compounds identified. The most interesting of these is the di-iodide, NaI_2, $3H_2O$; since polyiodides containing an even number of iodine atoms are unlikely, it has been suggested that this compound may be NaI, NaI_3, $6H_2O$, i.e. a molecular compound of two iodides containing odd numbers of halogen atoms. The compounds KI_6CNS, $4C_6H_6$; $KI_3C_6H_6$; $KI_52C_6H_6$; RbI_7, $4C_6H_6$ and RbI_8, $4C_6H_6$, are among the recent discoveries, while thallium forms Tl_6I_8 and TlI_3.

The fact that the freezing point of an alkali iodide solution is not lowered when iodine is dissolved in it shows that a compound is formed: The number of molecules or ions in solution remains unaltered, since the iodine molecules added merely convert I ions into I_3 ions. The constitution of these polyiodides is not very clear. The iodine molecule may be added on to the iodine ion as indicated thus, $[I(I_2)]'$.

The property of forming polyiodides is connected with the volume of the cation. Caesium, with the largest atomic volume of any metal, forms them most easily, and

[1] Briggs and co-workers, *Z. anorg. Chem.*, 1939, 242, 325; *J. Physical Chem.*, 1940, 44, 322, 350; Cheeseman, Duncan and Harris, *J. Chem. Soc.*, 1940, 837.

the other alkali metals form them to a less extent as the atomic volume decreases. The alkaline earths, the atomic volumes of which are still considerable, show a tendency to form polyiodides, which disappears almost entirely in the heavy metals. When a heavy metal forms a complex radical of large volume, *e.g.* $[Ni(NH_3)_6]''$, $[Co(NH_3)_6]'''$, well-defined polyiodides are formed. Further, polyiodides are also formed with organic bases of large molecular volume, such as the alkaloids, and with tri-phenylmethyl $[(C_6H_5)_3 : C]'$, which take up more than one molecule of iodine. These solid polyiodides are probably solid solutions of iodine in the lower polyiodide ; with the heavier cations the solubility usually decreases.

The tribromides $CsBr_3$, $RbBr_3$ and NH_4Br_3 as well as $CsBr_4$ and $2KBr_6 \cdot 3H_2O$ are also known, but no polychlorides. There are, however, a considerable number of alkali polyhalides containing several different halogens,[1] *e.g.* :

$CsIBr_2$	$RbIBr_2$	$KIBr_2$	$RbFICl_5$
$CsICl_2$	$RbICl_2$	$KICl_2$	$CsFICl_8$
$CsBrCl_2$	$RbBrCl_2$	NH_4IBr_2	
$CsClBr_2$	$RbClBr_2$	NH_4ClBr_2	

These crystallise easily from aqueous solutions of their components and are lighter-coloured when they contain less of the heavier halogens. The colour gradates from the black of the polyiodides through dichromate-orange to the pale yellow of the brom-chlorides. The stability of some of these compounds is very considerable (CsI_3 has a decomposition pressure of one atmosphere only at 250°), particularly when an iodine atom is present, but rapidly diminishes when only bromine or bromine and chlorine are there. It disappears completely with the last bromine atom, as no polychlorides are known.[2] When a polyhalide, is exposed to air or heated it becomes white, and the simple alkali halide containing the most negative of the halogen atoms is left behind.

A particularly fine group of polyhalides has the general formula $MICl_4$. These pentahalides can be regarded either as complex iodides, $M[I(Cl_4)]$ (and ICl_4 groups are present in the crystals), or as additive compounds of the chloride with iodine trichloride, ICl_3, thus : $M[Cl(ICl_3)]$. They are formed in various ways from the aqueous solutions of their components, *e.g.* from chloride and iodine chloride, or from iodide and chlorine, or from iodate and hydro-chloric acid. They exist as fine yellow needles which on exposure to the air give off iodine trichloride, leaving the chloride. The free chloroiodous acid, $HICl_4 \cdot 4H_2O$, is obtained as orange yellow tables when chlorine is passed through a suspension of iodine in concentrated hydrochloric acid This class of polyhalide is by far the largest, and includes salts of Na and Li,[3] and even of the heavy metals.[4] The polyhalides of the heavy metals contain much water of crystallisation

[1] Wells and Wheeler, *Z. anorg. Chem.*, 1892, **1**, 442.
[2] Ephraim, *Ber.*, 1917, **50**, 1069.
[3] Wells and Wheeler, *Z. anorg. Chem.*, 1892, **2**, 259.
[4] Weinland and Schlegelmilch, *Z. anorg. Chem.*, 1902, **30**, 140.

which cannot be removed without driving off some of the halogen. This behaviour is typical of the general condition that complex formation in one ion is usually accompanied by an increase in complexity in the other ion. The addition of iodine trichloride to the anion is only possible when the cation is hydrated, and *anhydrous* double salts of heavy metals with iodine trichloride do not therefore exist.

Halides of the Univalent Heavy Metals

The most notable characteristic of the halides of univalent Cu, Ag, Au, Hg and Tl is their low solubility in water. Their insolubility increases with increasing atomic weight of the halogen, and although the fluorides are usually somewhat soluble, the chlorides are mostly insoluble. The solubility of the cyanides and thiocyanates is variable; thallous cyanide is easily soluble, but the other cyanides are insoluble. The following table gives the solubility of the slightly soluble halides in moles per litre of saturated solution, determined from measurements of electrical conductivity or electromotive force. The solubility of the sulphides is included for comparison.

	Cl	Br	I	CN	CNS	S
Ag (25°) .	1.5×10^{-5}	7.15×10^{-7}	1.08×10^{-8}	2.2×10^{-6}	1.08×10^{-6}	1.0×10^{-17}
Cu (25°) .	1.1×10^{-3}	2.0×10^{-4}	2.25×10^{-6}		1.10×10^{-13}	3.5×10^{-6}
Hg$_2$.	5.5×10^{-14}	6.5×10^{-18}	2.9×10^{-21}	2.7×10^{-35}	1.1×10^{-16}	8.3×10^{-42}
Tl (18°) .	1.61×10^{-2}	1.64×10^{-3}	1.92×10^{-4}	easily sol.	1.2×10^{-2}	

The alteration in solubility when complexes are formed is discussed on p. 248.

Preparation.—If the low solubility is made use of, the preparation of these halides is simple, for example silver and thallium halides are almost exclusively prepared by double decomposition. Others are made synthetically, *e.g.* mercurous iodide, which can be made by grinding mercury and iodine in the proper proportions. The halogen may also be supplied from a metallic halide. Thus, mercurous chloride and bromide can be made by subliming mercuric chloride or bromide with metallic mercury: $Hg + HgCl_2 \longrightarrow Hg_2Cl_2$. Cuprous chloride and bromide are prepared by the analogous wet reaction when copper is boiled with cupric chloride solution: $Cu + CuCl_2 \longrightarrow 2CuCl$. The cuprous chloride dissolves in concentrated hydrochloric acid or salt solution, owing to formation of complex compounds—[CuCl$_2$]H or [CuCl$_2$]Na—which are decomposed by water, and the cuprous chloride is precipitated in minute crystals.

Some of these halogen compounds are formed by decomposition of higher halides, some of which even decompose spontaneously. If, for example, auric hydroxide is dissolved in hydrocyanic acid, aurous cyanide, AuCN, is formed instead of the auric salt, Au(CN)$_3$. Cupric salts also give lower cyanides with evolution of

cyanogen when treated with potassium cyanide and gently warmed: $Cu(CN)_2 \longrightarrow CuCN + CN$. Cuprous iodide is similarly formed with liberation of iodine: $CuI_2 \longrightarrow CuI + I$, but part of the iodine remains dissolved in the cuprous iodide, probably forming a compound which contains both uni- and bivalent copper. Such a compound is certainly formed in the dark brown solutions obtained on exposing a hydro-chloric acid solution of cuprous chloride to the air. Some higher halides decompose only on heating; thus $AuCl_3$ decomposes to $AuCl$ at 170°-200°, $AuBr_3$ to $AuBr$ at 115°, while AuI_3 decomposes at room temperature. Consequently $Au(OH)_3$ gives aurous iodide with hydriodic acid, but as the lower iodide is an endothermic compound (heat of formation $= -5.5$ cal.) it decomposes to some extent into gold and iodine. This decomposition also occurs in the chloride and bromide, but the liberated halogen oxidises the aurous salt to the auric condition: $3AuCl \longrightarrow AuCl_3 + 2Au$, and so the total weight remains unchanged. Therefore AuI does not simply dissolve in potassium iodide but is partly decomposed, with precipitation of the metal. The decomposition, however, proceeds only up to a certain concentration of iodine in the solution, and if some free iodine is previously dissolved the aurous iodide dissolves without separation of gold. The dissociation pressure can be measured, since it is the osmotic pressure of the iodine in a solution of iodine in potassium iodide which just permits aurous iodide to be dissolved without decomposition. This osmotic pressure is considerable, and at room temperature is 95 per cent. of that of a saturated solution of iodine in carbon tetrachloride.

In other cases strong reducing agents are necessary. Thus the dark brown cupric thiocyanate, although very slowly reduced spontaneously to the white cuprous salt, is reduced much more rapidly if sulphur dioxide or ferrous sulphate is added. Cupric chloride is more difficult to reduce, and chlorine is lost only at a red heat. But on addition of reducing agents such as bisulphites, stannous chloride, hydrazine, phosphine or hypophosphorous acid the reaction is complete in aqueous solution, and the white precipitate of cuprous chloride is rapidly formed. The same reducing agents also reduce mercuric to mercurous chloride, but stannous chloride also reduces the mercurous salt, with formation of metallic mercury—pure mercurous chloride is formed only when the mercury salt is in excess:

$$\text{I. } 2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4.$$

$$\text{II. } Hg_2Cl_2 + SnCl_2 \longrightarrow 2Hg + SnCl_4.$$
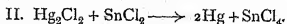
The reduction of mercuric chloride by oxalates is interesting—

$$2HgCl_2 + M_2C_2O_4 \longrightarrow 2MCl + 2CO_2 + Hg_2Cl_2,$$
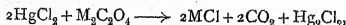
as it proceeds hardly at all in the dark, and the rate is so much

influenced by the intensity of the illumination that it can be employed as a chemical actinometer.[1]

Properties.—The halides of the univalent heavy metals crystallise mostly in the regular system; the silver and thallium salts in octahedra, the copper salts in tetrahedra. Owing to their low solubility the precipitation of these salts is so rapid that most of them are apparently amorphous. Many of them appear first in the colloidal form and only crystallise after some time. This is especially noticeable in the silver salts; their colloidal solutions remain stable for some time, and even after settling the curdy precipitate only slowly becomes crystalline. Many of the salts of this group, when washed with pure water after crystallisation, pass readily into the colloidal condition; *e.g.* thallous iodide, which is used for the quantitative determination of thallium, often passes suddenly through the filter when a certain stage in the washing is reached. When the halogen salts are slowly deposited from solution they can be obtained in crystals without passing through the colloidal condition. If, for example, a solution of silver chloride in ammonia or in hydrochloric acid is slowly evaporated, the complex formed with NH_3 or HCl breaks up for lack of these substances and the silver chloride is deposited in octahedra. Similarly cuprous chloride, resulting from the slow reduction of cupric chloride with hypophosphorous acid, is quite granular. These halides can also be obtained crystalline after fusion, provided no decomposition occurs. The melting and boiling points are as follows:

				Cl	Br	I
Cu	.	.	m.pt.	$434°$	$480°$	$590°$
			b.pt.	ca. $1000°$	ca. $900°$	ca. $765°$
Ag	.	.	m.pt.	$455°$	$422°$	$552°$
Tl	.	.	m.pt.	$451°$	$463°$	$446°$
			b.pt.	$708°$	...	$800°$

The mercurous halides sublime without melting—the chloride at $383°$; the gold salts decompose when heated, leaving the free metal. The vapour density of the salts which do not decompose on heating is normal.

The colour of these salts is white or pale yellow to orange. The gold salts are of the latter colour, the iodide being the deeper yellow. The green colour of mercurous iodide is due to its partial decomposition into mercuric iodide and free mercury. The bright yellow mercurous and thallous iodides become red on heating and assume a different crystalline form, but revert to their original colour on cooling. Silver iodide exists in three crystalline forms as well as the colloidal form: light yellow crystals of the hexagonal system, stable below $146°$, a

[1] Eder, *Ber. Wien. Akad.* (2), 80a, Oct. 1897; Roloff, *Z. physikal. Chem.*, 1894, 13, 329.

golden yellow form belonging to the regular system, stable above 146°, and a third form which exists only at low temperatures and under high pressure.

Crystal Structure.—The crystal structure of the halides of the univalent heavy metals is very variable owing to their allotropy. Five different types have so far been observed. Silver chloride and bromide are of the rock salt type (p. 299), thallium chloride is of the caesium chloride type (p. 239), while the three cuprous halides have the same structure as diamond (p. 21), which is also found in zinc blende, ZnS. The copper atoms occupy the corners of the cube and the halogen atoms form the inscribed tetrahedron. One of the three forms of silver iodide shows a complicated structure, of which the best-known example is wurtzite, a form of ZnS (p. 884); another has the zinc blende structure, while the third is cubic (above 146°). It is probable that when the various allotropic forms are studied by the X-ray method they will give examples of the above structures in all the halides.

Complex Formation.—The solubility of the halides of the univalent heavy metals is lowered by the presence of small quantities of salts with a common ion, but large quantities of alkali halides or halogen acids increase the solubility owing to the formation of complexes. This increase in solubility is less marked in the mercury salts, though it is still perceptible; the mercurous salts in general are not greatly inclined to form complexes.

It is possible to isolate some of these complexes of acid and halide. Thus the acid fluorides of Hg, Tl and Ag can be obtained, that of the last having the formula $AgF.3HF$, that is $[AgF_4]H_3$. The chloro-acids such as $[CuCl_2]H$ are less stable, and those of the other halogen acids still more liable to decompose; but their salts (double halides), particularly those with the alkali metals, are easy to prepare, as they crystallise from solutions of their components. The double halides of univalent gold can also be obtained by heating the corresponding compounds of tervalent gold : $KAuCl_4 \longrightarrow KAuCl_2 + Cl_2$. The halogen salt of the univalent metal is precipitated when the solution is diluted with water, as the complex is thereby dissociated and the free metal and halogen ions form the halide once again.

The complexes formed by hydrocyanic acid are particularly stable, and are produced when potassium cyanide is added to a solution of a salt of the metal in sufficient excess to redissolve the first precipitate of simple cyanide : $MCN + KCN \longrightarrow [M(CN)_2]K$. These compounds are so little decomposed on dilution that no cyanide is precipitated. The small concentration of metal ions in these solutions makes them give a bright coating in the electro-deposition of the metal (p. 212) —silvering and gilding. The few metal ions that exist do not respond to the usual reagents, and, indeed, the precipitates which might be formed are soluble in KCN; *e.g.* silver chloride, which forms the

complex $[Ag(CN)_2]'$, and thus reduces the concentration of metal ions below that required by the solubility product of AgCl. These complexes are known in the solid state only for the metals of the first sub-group of the periodic system (Ag, Cu and Au), those of Tl and Hg being less stable. Complex thiocyanates are also known, but the complexes are not so definite, and the insoluble thiocyanates are not readily dissolved by excess of potassium thiocyanate. Complex thiosulphates of silver and of univalent copper are known in the solid state and, in solution, are not precipitated by chloride ions.

In these complexes the heavy metal is combined with negative radicals and thus forms part of the anion. There are also strong complexes in which the metal is part of the cation. With silver and copper, and to a less extent with the other metals of this group, complex cations are formed with ammonia, of the type $[M(NH_3)_2]'$. The aqueous solution does not contain enough metal ions to give a precipitate with chloride ions, but with iodide ions a precipitate is produced, as silver iodide is less soluble than the chloride (p. 245). Once the precipitation begins the few free metal ions in equilibrium with the complex are rapidly used up, and more of the complex dissociates to maintain the equilibrium. Precipitation thus goes on until the whole of the complex is used up. Either the precipitation does not occur at all (Cl' ions in ammoniacal silver solution) or it is complete (I' ions in that solution). Consequently, silver chloride is soluble in ammonia while the iodide is not.

The ammines of the silver, gold and copper salts are obtained in the solid state when ammonia gas is passed over the solid halide. Each atom of the metal takes up three molecules of ammonia, $[Ag(NH_3)_3]'$, $[Au(NH_3)_3]'$, $[Cu(NH_3)_3]'$, but in aqueous solution the complex ions certainly contain less ammonia.

The compounds formed by these chlorides with organic amines, sulphides, nitriles, and with esters of phosphorous acid when dissolved in these media are similar to the complexes with ammonia. The remarkable complex $AgCl.AgNO_3$ is only partly decomposed by the addition of small quantities of water.

Decomposition.—The separation of free halogen is a very common form of decomposition in this group of halides; but when the compound can be oxidised the halogen oxidises a further portion instead of appearing in the free state, *e.g.* $2HgI = HgI_2 + Hg$. When the more halogenated compound is easily reduced an equilibrium is established, *e.g.* $3M' \rightleftharpoons 2M + M'''$, as has been discussed already in the reactions of the iodides of gold (p. 246). These actions indicate that the cuprous and aurous halides are more easily reduced (*i.e.* split off halogen more easily) than the cupric or auric compounds. When no higher halide exists the halogen is actually set free, as with silver chloride.

The decomposition of the gold halides, and of some of the copper compounds in which the metal is set free, is accelerated by heat, and

some or all of the halogen is used up in oxidising the original compound to the higher state. Hence the aurous halides cannot be kept for long in the pure state and are found to contain metallic gold and auric salts: $3Au^{\cdot} \rightleftharpoons Au^{\cdots} + 2Au$. Even the double halides of univalent gold (e.g. $KAuCl_2$) decompose in this way in solution although they are fairly stable in the solid state; for the complex is partly dissociated in solution and the insolubility of the metal upsets the equilibrium.

Mercurous iodide decomposes spontaneously into the mercuric salt and free mercury, becoming green at first and later on darker in colour. The chloride behaves towards some reagents as if it were a mixture of mercuric chloride and metallic mercury, as for example with ammonia, when the darkening due to separation of mercury is accompanied by the formation of $ClHgNH_2$. According to Feigl,[1] $Hg_2Cl(NH_2)$ is first formed, which then breaks down into Hg and $ClHgNH_2$.

Mercuric salts and mercury are also produced when the mercurous compounds are heated. The vapour density of mercurous chloride at 400° shows decomposition of Hg_2Cl_2 into two molecules, and one might assume that the reaction $Hg_2Cl_2 \rightleftharpoons 2HgCl$ takes place; but a gold leaf placed in the vapour is at once amalgamated (Odling), and mercury vapour can be separated by fractional diffusion. It is therefore more probable that the decomposition occurs thus: $Hg_2Cl_2 \longrightarrow HgCl_2 + Hg$. The normal density for Hg_2Cl_2 is, however, obtained if the mercurous chloride is subjected to prolonged desiccation (Baker). Mercurous bromide behaves in the same way.

Decompositions of this type can often be traced to rearrangements within the molecule. These halides are mostly bimolecular; cuprous chloride even at 1560° has a density corresponding to the double formula (V. and C. Meyer), and the bromide is also polymerised in solution in ethyl sulphide and at 900°-1000°, though in pyridine solution it shows the simple formula owing to formation of complexes with the solvent. Cuprous iodide, however, has the formula CuI at the temperature mentioned above. The bimolecular condition of the mercurous compounds has also been proved beyond doubt. These substances may therefore be assumed to be salts of complex halogen acids; $(CuCl_2)_2$ as the copper salt of chlorocuprous acid, $[CuCl_2]Cu$ and the mercurous salt similarly $[HgCl_2]Hg$. But this assumption implies a difference of function of the two atoms of mercury in the molecule, and is not necessary. A second possibility is indicated by the formula $[Hg_2Cl]Cl$, but it is simpler to assume that polymerisation occurs and that the affinity of the chlorine atoms is divided between two mercury atoms in such a way that each occupies half the total affinity of the chlorine atom. This corresponds with the electronic formula:

$$
\begin{array}{ccc}
 & Cl & \\
Hg & & Hg \\
 & Cl & \\
\end{array}
$$

[1] Z. anal. Chem., 1925, 67, 134.

On this assumption decomposition can occur in the two following ways:

$$\text{Hg} \text{------} \text{Cl} \qquad \qquad \text{Hg} \text{------} \text{Cl}$$

$$\longrightarrow \text{HgCl}_2 + \text{Hg} \quad \text{or} \qquad \longrightarrow 2\text{HgCl}.$$

$$\text{Cl} \text{------} \text{Hg} \qquad \qquad \text{Cl} \text{------} \text{Hg}$$
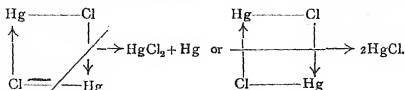
Ogg has studied these equilibria in the mercurous salts,[1] and showed that bivalent mercury ions exist in solutions of mercurous salts in considerable quantity. He suggested as a result of his work that these were double mercury ions $\text{Hg}_2^{\cdot\cdot}$, but they might be single mercury ions $\text{Hg}^{\cdot}$ related to the negative ions HgCl_3'. The mercurous salts can be formed by shaking solutions of mercuric salts with mercury, and according to the assumption of the structure of the ion this process is represented as

$$\text{I.} \quad \text{Hg}^{\cdot\cdot} + \text{Hg} \rightleftharpoons 2\text{Hg}^{\cdot} \qquad \text{or} \qquad \text{II.} \quad \text{Hg}^{\cdot\cdot} + \text{Hg} \rightleftharpoons \text{Hg}_2^{\cdot\cdot}.$$
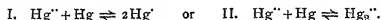
The law of mass action requires

$$\text{I.} \quad \frac{\text{Hg}^{\cdot\cdot} \times \text{Hg}}{\text{Hg}^{\cdot 2}} = K \qquad \text{or} \qquad \text{II.} \quad \frac{\text{Hg}^{\cdot\cdot} \times \text{Hg}}{\text{Hg}_2^{\cdot\cdot}} = K,$$

and thus in the first case the constant depends on the second power of the concentration of the mercurous ions, in the second case on the first power. The latter was undoubtedly in agreement with the experimental results, and thus we must assume the presence of bivalent ions in solutions of the mercurous salts. That these are $\text{Hg}_2^{\cdot\cdot}$ ions, as Ogg assumed, and not $(\text{HgClHg})^{\cdot}$ ions has been shown[2] by experiments on conductivity and transport numbers in solutions of mercurous nitrate.

A study of the crystal structure of mercurous chloride by Mauguin,[3] using the X-ray method, shows that both arrangements of the atoms are present in the solid state. The grouping of the atoms in the prismatic crystals is as follows:

$$\begin{array}{cccccc} \text{Hg} & \text{Hg} & \text{Cl} & \text{Cl} & \text{Hg} & \text{Hg} \\ \text{Cl} & \text{Cl} & \text{Hg} & \text{Hg} & \text{Cl} & \text{Cl} \end{array}$$
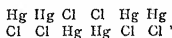
so that both (Hg_2) groups, *i.e.* $\begin{array}{cc}\text{Hg} & \text{Hg} \\ \text{Cl} & \text{Cl}\end{array}$ corresponding to $\begin{array}{cc}\text{Hg}-\text{Hg} \\ | \quad | \\ \text{Cl} \quad \text{Cl}\end{array}$ and $\begin{array}{cc}\text{Hg} & \text{Cl} \\ \text{Cl} & \text{Hg}\end{array}$ groups

corresponding to the cyclic formula above, are to be found there. The affinity of the Hg atoms for the Cl atoms differs in the two forms of grouping, but not to any great extent, the distance between the atoms in the horizontal layers being $3 \cdot 15 \times 10^{-8}$ cm., while the atoms vertically beneath one another are $2 \cdot 72 \times 10^{-8}$ cm. apart.

The decomposition of the univalent halides of gold, copper, etc., into a higher halide and free metal does not take place when a sufficient quantity of the higher halide is already present in solution. There is, in fact, an equilibrium between $\text{Cu}^{\cdot}$ and $\text{Cu}^{\cdot\cdot}$ thus: $2\text{Cu}^{\cdot} \rightleftharpoons \text{Cu}^{\cdot\cdot} + \text{Cu}$ and hence $\dfrac{\text{Cu}^{\cdot\cdot}}{\text{Cu}^{\cdot 2}} = k$. If, therefore, cuprous salt is added to a solution which contains $\text{Cu}^{\cdot\cdot}$ ions it will dissolve unchanged until the equilibrium is established, but if further quantities of the cuprous salt are then added, some breaks up to give more $\text{Cu}^{\cdot\cdot}$ ions, which then react with more of the cuprous salt; the metallic copper is a necessary by-product

[1] *Z. physikal. Chem.*, 1898, **27**, 285.   [2] *Z. anorg. Chem.*, 1924, **133**, 55.
[3] *Compt. rend.*, 1924, **178**, 1913.

of the decomposition of the cuprous salt. The cuprous salt will only appear as a solid phase when the square of its solubility product is less than the solubility product of the cupric salt; otherwise the cupric salt will separate out before the solution is saturated with cuprous salt, and any solid cuprous salt will go into solution and form more cupric salt. In practice, only the insoluble cuprous salts (halides, thiocyanate, sulphide) can be isolated from aqueous solution. At higher temperatures the ionisation of cupric salts is increased, and hence more $Cu^{.}$ ions can be retained in equilibrium, so that hot concentrated solutions of cupric salts dissolve metallic copper, but on cooling copper is deposited with the cupric salt.

The tendency for $Cu^{..}$ ions to pass spontaneously into $Cu^{.}$ ions is considerable. In the presence of weak anions like the cyanide ion the equilibrium $Cu^{..} + 2CN' \rightleftharpoons Cu^{.} + CN' + CN$ lies well to the right. When a strong anion is present and the ionisation thus increased, the reaction proceeds to the left, e.g. $CuCl_2 \longleftarrow CuCl + Cl$, and separation of the cuprous salt occurs only when this is very insoluble like CuI. CuI_2 breaks up spontaneously into CuI and I as the equilibrium $CuI_2 \rightleftharpoons CuI + I$ is disturbed by the separation of even minute quantities of CuI, and the reaction proceeds to completion on the right-hand side. The calculations of electro-affinity and solubility product made by Bodländer and Storbeck[1] confirm the views given above.

The energy required to effect oxidation can be used as a measure of the stability of the cupric and cuprous conditions. The electric potential differences give a numerical measure of the energy: $Cu \longrightarrow Cu^{.} = +0.52$ volt, $Cu \longrightarrow Cu^{..} = +0.34$ volt, $Cu^{.} \longrightarrow Cu^{..} = +0.18$ volt. It can be seen that a smaller expenditure of energy is required to convert metallic copper into $Cu^{..}$ ions than is required to convert it into $Cu^{.}$ ions. This apparently paradoxical fact is a special case of Luther's Rule (p. 376).

The equilibria $Hg + Hg^{..} \longrightarrow Hg_2^{..}$ and $2Au + Au^{...} \longrightarrow 3Au^{.}$ can be considered in the same way as that of the copper salts.

The Action of Light.—The liberation of halogen is promoted by the action of certain kinds of radiation, and in consequence most of the compounds of this class undergo decomposition and darkening when exposed to light. The white salts are turned violet, the yellow ones green. The violet rays of the spectrum are most active in decomposing silver chloride, and the effect can be followed right into the ultra-violet region, while it lessens and finally ceases towards the red end. X-rays and the α-rays also have a strong decomposing effect. Iodides are more susceptible to light than chlorides and bromides, but while thallous fluoride blackens in sunlight, silver fluoride and thiocyanate, like cuprous cyanide and thiocyanate, are not sensitive to light; cuprous chloride is affected only when it is damp, and

[1] Z. anorg. Chem., 1902, 31, 458.

the presence of cupric salt also inhibits the reaction owing to the alternative decomposition treated in the previous paragraph. The effect of light can therefore proceed up to a condition of equilibrium, since eventually the liberated halogen oxidises the cuprous salt to the cupric state.

The decomposition of the silver salts by light has been most studied owing to its wide application in photography. Silver chloride first becomes lilac in colour and then passes through violet to a slate grey. A distinct smell of chlorine is developed at the same time, and a loss of weight occurs.[1] The loss of weight is most rapid at the commencement of the action, and after exposure for half a year amounts to more than 8 per cent. If the salt is in a closed vessel the evolution of chlorine does not proceed to this extent, and in the dark the reaction is reversed; in fact, the equilibrium pressure of chlorine can be measured if the silver chloride is exposed to light while immersed in chlorine water of various concentrations. Blackening continues below a certain concentration, but above that concentration of chlorine it no longer takes place.[2]

The Subhalides.—The chemical nature of the coloured products of the action of light has been the subject of much research. It was originally supposed that so-called subhalides were produced with formulae of the type Ag_2Cl, and later that solid solutions of these subhalides in the unchanged silver halides were formed. It is now commonly accepted that the coloured substances are colloidal solutions of the free metal in the halide.

The subhalide theory was supported by the isolation of crystalline forms of apparently constant composition. Thus Guntz obtained a bronze crystalline powder on adding finely divided silver to a solution of silver fluoride; it can also be made by the electrolysis of AgF solutions. It has the composition Ag_2F and is certainly a definite compound, but it is decomposed by the moisture of the air when no excess of silver fluoride is present, and at 90° splits up thus : $Ag_2F \longrightarrow Ag + AgF$. This subfluoride was supposed to be converted into the subchloride on heating with PCl_3 at 140°. Highly coloured but well-formed crystals of a subchloride were also obtained when solutions of silver chloride in ammonia or hydrochloric acid were allowed to evaporate in the light; but here it may be supposed that the silver chloride which separates subsequently undergoes the same transformation as when it is amorphous. It is possible to obtain subhalides of the most varied composition by treating colloidal solutions of metallic silver with different quantities of chlorine or bromine in water, when the solution first changes colour and then precipitates the subhalide as a powder. The substance which has the composition Ag_2Cl is fawn coloured; with less chlorine it is greenish. With increasing chlorine content the colour passes through the series

[1] *Cf.* E. J. Hartung, *Phil. Mag.*, 1922, vi., **43**, 1056.
[2] Luther, *Z. physikal. Chem.*, 1899, **30**, 628.

yellow red $\longrightarrow$ purple red $\longrightarrow$ rose $\longrightarrow$ pale pink $\longrightarrow$ lilac, and finally white, when the formula of the ordinary chloride is attained. On investigating the existence of a subchloride by the method of electrical potential a distinct break in the curve was found to occur at the composition Ag_2Cl; but doubt has been thrown on this observation.[1] In any case colloidal silver and the chloride or bromide are miscible in all proportions.

Photohalides. — The mixtures which contain more halogen than Ag_2X are known as photohalides, and have the remarkable property of adjusting their colour to that of the light to which they are exposed. Thus they turn blue in a blue light, red in a red light, and the spectrum can be reproduced on them in colour. They cannot, however, be used in colour photography as they do not reproduce white. The various colours are in all probability due to particles of various sizes.

The bromide and iodide of silver are more sensitive to light than the chloride. The sub-bromide is a brownish-violet powder, while the photo-bromides are deep lilac to violet in colour. After a brief exposure to light the grains of silver are too small to be detected, but they can be made larger by artificially crystallising out silver from a solution in their presence. They then act as crystal nuclei on which most of the new silver is deposited. This "development" is brought about by the use of reducing agents such as pyrogallol, ferrous sulphate, etc. The silver solution used in photography is a colloidal solution of silver halide in gelatin, which is spread on the plate, or similar solutions in collodion are used, making diffusion more difficult and thus giving a sharper image. Reduction commences on those particles which have already been partly decomposed by the light, and the change ends visibly on the outer borders of these particles. This effect is commonly observed in reactions in solids—when a small quantity has been changed the action proceeds much more readily. (Thus the efflorescence of a crystal is accelerated by a particle of anhydrous salt, although a well-formed crystal can be kept for some time in a dry atmosphere if it is not scratched.) In order that the action of the light in regulating development may be effective, it is essential that the grains of silver halide in the emulsion be not too small. The emulsion is therefore "ripened" by digesting it for some time at 40°, when the larger grains grow at the expense of the smaller ones, as the latter are more soluble. The exposed plate has an olive green colour; it is unnecessary and even harmful to expose to light so much that visible blackening occurs, for the phenomenon known as "solarisation" takes place, and a positive image which cannot be developed is formed instead of a negative. After development the unchanged silver halide is dissolved out with thiosulphate (see p. 558) and the negative image thus fixed.

Light has a secondary effect in breaking up the grains of silver

[1] Baur, *Jahrb. der Photogr.*, 1904, 60.

halide, for the liberated halogen recombines with some of the free silver and thus forms new grains of halide. If a portion of a silvered glass plate is first exposed to iodine vapour and then to light, free silver is found on the iodised portion and the mirror of silver is converted into silver iodide. The iodine moves from the exposed to the unexposed part, where it is fixed by the silver present.

Daguerre's process was the original method of photography. A plate of silver was first iodised and then exposed to light, when the free silver formed could be amalgamated with mercury vapour and thus made visible. A Daguerreotype plate can be developed in the modern way by using a mixture of silver nitrate and ferrous sulphate, when the small quantity of silver produced is deposited on the illuminated portions. The ferric salt formed soon prevents further deposition of silver, and in order that the action may proceed it must be converted into complex ions.

The toning of a silver image is brought about by immersing the paper in a solution of a salt of a metal more noble than silver, e.g. gold or platinum. The ions of the metal in solution give up their charge to the silver, which thus passes into solution, while the other metal takes its place on the paper: $4Ag + Pt^{\cdots\cdots} \longrightarrow 4Ag^{\cdot} + Pt$.

It has been suggested that when a silver bromide is exposed to light the negative bromion loses an electron which is picked up by the silver ion, thus forming atoms of bromine and silver. It has been shown that silver bromide precipitated in presence of excess of silver nitrate is more sensitive to light than that made with excess of potassium bromide. Fajans and Frankenburger[1] explain this on the ground that in the first case the halide is coated with adsorbed silver ions, in the second with adsorbed bromide ions. This is in agreement with the well-known fact that silver halides precipitated from excess silver solution give a positive sol, while when made from excess halide a negative sol is obtained. When the surface is covered with negative bromions the more deeply embedded bromions will have greater difficulty in transferring their charges to the surface silver ions than when there is an excess of silver ions in the surface due to adsorption. These effects are applied in the use of *adsorption indicators* in volumetric analysis, e.g. eosin is added to the iodide solution which is to be titrated with silver nitrate. At first, iodide ions are adsorbed on the precipitated silver iodide, but when the end-point is reached, silver ions are adsorbed, which form silver eosinate with the dyestuff. This is adsorbed on the precipitate and a characteristic colour change ensues.

Univalent Halides of Polyvalent Metals.—Metal halides usually include examples of the very lowest (and incidentally of the very highest) of the valencies exhibited by a given metal. Although the subhalides of such metals as silver may be mixtures of the metal with a normal

[1] *Z. physikal. Chem.*, 1923, 105, 255.

halide (p. 253) the subhalides of the alkaline earth metals do not contain free metal (p. 259) and that of samarium contains that metal in the bivalent instead of the tervalent state. The ammines of the latter subhalide are quite different from those of the SaX_2 type.[1] Indium, like thallium, also forms univalent halides, InCl, InBr, InI, but such compounds of gallium are unknown.

Double cyanides of manganese, iron, nickel and cobalt can be prepared in which these metals are univalent. The univalent manganese compound is obtained by the reduction of potassium manganese cyanide with Al and NaOH or KOH. The compounds $Na_5Mn(CN)_6$ and $K_5Mn(CN)_6$ are obtained as colourless crystals; $K_2Mn(CN)_3$ can be prepared similarly or by reduction with Devarda's alloy.[2] These substances are powerful reducing agents; their aqueous solutions evolve hydrogen, bleach dyes, and reduce salts of Pb, Cd and Bi to the metals. The univalent nickel compound, $K_2Ni(CN)_3$, forms a dark red oily substance when higher double cyanides are reduced with potassium amalgam or electrolytically.[3] This double cyanide, like the bivalent cobalt compound, forms addition compounds with carbon monoxide (p. 790). By treatment with acid, NiCN is formed, which gives the unstable compound NiCN.CO with CO. The univalent cobalt compound, made in the same way, has not been isolated from solution—it is of a brownish-green colour.[4] Reduction of $K_2(Pt, Pd)(CN)_4$ with sodium amalgam[5] gave evidence of colourless solutions of Pt^I and Pd^I. $K_2Pd(CN)_4$, $K_2Ni(CN)_4$, $NiSO_4$, $Ni(OAc)_2$, $RuCl_3$ and $RhCl_3$ are readily reduced by NaH_2PO_2 to solutions containing the metals in the univalent condition, but $K_2Pt(CN)_4$, $K_4Rh(CN)_6$, $K_3Rh(CN)_6$, $K_3Ir(CN)_6$ and $K_4Os(CN)_6$ are either unaffected or are only partially reduced.[6]

According to Manchot, univalent compounds of Fe, Mn, Co and Ni are to be found also in the addition products formed by compounds of these metals (e.g. mercaptides) with nitric oxide (cf. p. 680).

[1] Klemm and Rockstroh, Z. anorg. Chem., 1928, 176, 181.
[2] Manchot and Gall, Ber., 1927, 60, 191; 1928, 61, 135.
[3] Bellucci, Z. anorg. Chem., 1914, 86, 88.
[4] Grube, Z. Elektrochem., 1927, 32, 561.
[5] Manchot and Schmid, Ber., 1930, 63 [B], 2782; Manchot and Lehmann, ibid., 2775.
[6] Manchot and Schmid, Ber., 1931, 64 [B], 2672.

CHAPTER X

HALOGEN SALTS: BI- AND TER-VALENT METALS

Halides of the alkaline earth metals—Of the other bivalent metals—Double halides—Solution—Hydrates—Ammines—Halides of tervalent metals—Their hydrates and complexes

Halides of Barium, Strontium and Calcium

CALCIUM chloride is a waste product in many technical processes, especially in the Solvay process for sodium carbonate. The ammonia is regenerated from the ammonium chloride solution by boiling with lime, and calcium chloride remains in solution. The other halides of this group are mostly made by one of the general methods given on p. 228 *et seq.*

There are very well-marked gradations in solubility in this group of halides; it increases from barium to calcium, and from chlorides to iodides. A saturated solution of barium chloride contains 25 per cent. of the salt at room temperature and 37 per cent. at 100°, while calcium chloride liquefies easily in the air, melts at 30° in its water of crystallisation, and even at 60° gives mixtures with water which contain 75 per cent. of the anhydrous salt. The differing solubility of the chlorides in alcohol (in which, incidentally, the iodides are all soluble) is used in the separation of barium from strontium and calcium; barium chloride dissolves in 7500 parts of absolute alcohol at room temperature, while calcium chloride dissolves readily and forms compounds with the alcohol.

The calcium salt also combines with water more readily than the barium compound—the former containing six molecules of water of crystallisation in its large clear crystals, while the latter forms small crystals with only two molecules of water. Anhydrous calcium chloride takes up water readily and is a favourite dehydrating agent. The porous mass obtained by dehydrating the hexahydrate without fusion is the most effective form. The hydration of the salt is accompanied by a considerable evolution of heat (21·7 Cals. per mole.), but the hydrate dissolves in water with absorption of heat (7·5 Cals.). The cryohydric point of water and the hexahydrate is as low as −55°, the eutectic mixture containing 8·5H_2O per mol. of $CaCl_2 . 6H_2O$.

This indicates the usefulness of crystalline calcium chloride in a freezing mixture.

The dehydration of these halides can be carried out without much decomposition, although commercial dehydrated calcium chloride is notably alkaline. The anhydrous halides fuse at higher temperatures, calcium chloride at 710°, barium chloride at 960°, and the iodides, like those of the alkali metals, at lower temperatures. Mixtures of the alkali and alkaline earth halides melt at still lower temperatures, and are used when it is desired to work with molten halides of the latter metals at as low a temperature as possible, *e.g.* in the manufacture of metallic calcium by electrolysis. Calcium fluoride is used in many metallurgical processes as a flux, for although it does not melt alone below 1330°, it causes other salts to melt to limpid liquids at much lower temperatures. This useful property is indicated by its name—fluorspar.

The fluorides of these metals, as has already been mentioned, differ from the other halides in being only slightly soluble in water. The beautiful cubes of native fluorspar are practically insoluble in water. But just as a gelatinous silicic acid which forms a colloidal solution in water exists in contrast to quartz, so when calcium fluoride is made by precipitation from an aqueous solution it appears as an opalescent jelly, difficult to filter. If the solution is sufficiently dilute it is not precipitated, but remains in the colloidal condition, and a sol containing several per cent. of the salt can be obtained by careful dialysis. On prolonged boiling the calcium fluoride is converted in part into tiny cubes, and similar crystals can be produced by methods of formation which operate slowly, as, for instance, when reacting solutions are allowed to diffuse into one another.

Fluorspar is so insoluble that aqueous acids much stronger than HF do not dissolve it. When treated with concentrated sulphuric acid, however, it is decomposed and the HF escapes. The fluorides of barium and strontium are similar to that of calcium, but are rather more soluble even in dilute acids; the unstable colloidal forms have therefore not been observed.
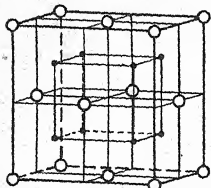
FIG. 36.—Crystal lattice of fluorspar.

The arrangement of the atoms in the fluorspar crystal, as determined by X-ray analysis, is shown in Fig. 36. The circles represent the positions of the calcium atoms, the black dots those of the fluorine atoms, and it can be seen that the former are situated at the corners and at the centres of the faces of the cube. If the cube is divided into eight equal cells the fluorine atoms are at the centres of these cells.

The cyanides and thiocyanates of the alkaline earths are soluble salts without any very characteristic properties.

Subhalides of the Alkaline Earths.—In these compounds the alkaline earths are apparently univalent, and substances of composition $CaCl$, CaI, CaF and $BaCl$ have been examined. They are unstable at ordinary temperatures and become rearranged into free metal and the normal halide, from which materials they can be synthesised at higher temperatures, thus :

$$\text{(low temp.) } CaCl_2 + Ca \rightleftharpoons 2CaCl \text{ (high temp.).}$$
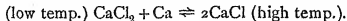
When the melts are quickly chilled to avoid the high rate of reversion at intermediate temperatures they remain metastable at room temperature.[1] The minimum temperatures to which the mixtures of metal and halide must be heated to produce the subhalides are : CaI, 780° ; $CaCl$, 800° ; CaF, 1400°.

The calcium subhalides are intensely coloured. The fluoride is brilliant red to orange yellow, the chloride reddish violet and the iodide brown. They are all well crystallised but hygroscopic, and react with water with rapid evolution of hydrogen, forming the hydroxide and ordinary halide of the metal. Barium subchloride, which is formed round the cathode when fused $BaCl_2$ is electrolysed, reacts in the same way and is said to be white.

Halides of the other Bivalent Metals

Formation.—Only magnesium chloride is obtained direct from the natural product. It occurs in the Stassfurt deposits (p. 237) as the hexahydrate (bischoffite), but is commoner in combination with other salts as double salts, whence it can be separated by processes of recrystallisation analogous to that used for carnallite (p. 237). The conditions under which magnesium chloride can crystallise by itself were investigated by van 't Hoff in his classical studies on the formation of the oceanic salt deposits.

The Stassfurt Deposits.—If one disregards the elements which occur in small quantities in the Stassfurt beds (Rb, Cs, Br, B, etc.), the deposits can be regarded as formed from various combinations of the following : Na, K, Mg, Cl, SO_4, H_2O. The varieties of compounds formed are very numerous, but the most important are :

$NaCl$, rock salt.	$3K_2SO_4$, Na_2SO_4, glaserite.
KCl, sylvine.	$MgSO_4$, H_2O, kieserite.
$MgCl_2$, $6H_2O$, bischoffite.	$MgSO_4$, $6H_2O$, hexahydrate.
$CaSO_4$, anhydrite.	$MgSO_4$, $7H_2O$, reichardite.
$CaSO_4$, $2H_2O$, gypsum.	K_2SO_4, $2CaSO_4$, $MgSO_4$, $2H_2O$, poly-
$3Na_2SO_4$, $MgSO_4$, vanthoffite.	halite.

[1] Wöhler and Rodewald, *Z. anorg. Chem.*, 1909, 61, 54.

KCl, MgCl$_2$, 6H$_2$O, carnallite.

CaCl$_2$, 2MgCl$_2$, 12H$_2$O, tachhydrite.
Na$_2$SO$_4$, thenardite.
Na$_2$SO$_4$, 10H$_2$O, Glauber's salt.
KCl, MgSO$_4$, 3H$_2$O, kainite.
K$_2$SO$_4$, MgSO$_4$, 4H$_2$O, leonite.

Na$_2$SO$_4$, MgSO$_4$, 4H$_2$O, astrachanite (blodite).
Na$_2$SO$_4$, MgSO$_4$, 2·5H$_2$O, löweite.
K$_2$SO$_4$, 2MgSO$_4$, langbeinite.
K$_2$SO$_4$, MgSO$_4$, 6H$_2$O, schönite.
Na$_2$SO$_4$, CaSO$_4$, glauberite.
K$_2$SO$_4$, CaSO$_4$, H$_2$O, syngenite.
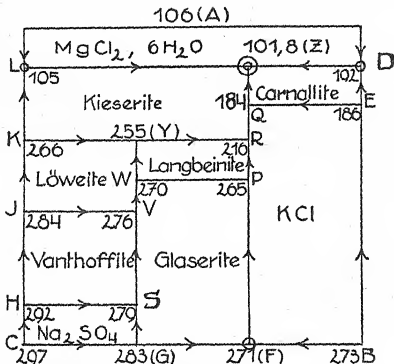
FIG. 37.

Each hydrate and double salt has its own sphere of stability limited by a maximum temperature and affected by the presence of other salts. The upper limits for a few compounds are:

	Glauberite	Schönite	Astrachanite	Leonite	Kainite
In absence of NaCl .	32·5°	47·5°	71°	89°	85°
In presence of NaCl .	18°	26°	59°	61·5°	83°

The conditions of decomposition and crystallisation become much more complicated when several other salts are present, and one of van 't Hoff's schemes[1] shown in Fig. 37 indicates the crystallisation from a solution containing certain of the salts in the deposits at 83° in the absence of calcium salts but with NaCl present to saturation.

The arrows in the figure show the direction of crystallisation; e.g. from an appropriate mixture, Na$_2$SO$_4$, vanthoffite, löweite, kieserite, and finally MgCl$_2$, 6H$_2$O, would be deposited in that order. Crystallisation then ceases, as indicated by the circle in the figure. The numbers show the vapour pressures of the solutions before and after the separation of the compound named in the space. These pressures are at points where, according to the phase rule, the system has no degrees of freedom, and where in consequence of alteration of any one condition one sort of crystal

[1] Ber. Berl. Akad., 1904, 518.

must disappear. In the diagram the substance which is used up is one of the two or three represented on areas meeting at the point considered. The relative positions of the areas show which salts can exist together as solid phases, namely, those represented by contiguous areas. Thus kieserite, löweite, and langbeinite can coexist in the solid state, but not kieserite, langbeinite and vanthoffite.

The relations are different at different temperatures, as is shown in the following smaller diagrams, which give the crystallisation data for the same mixture at various lower temperatures.

25°

Fig. 38.

27°5

Fig. 39.

49°

Fig. 40.

61°5
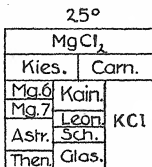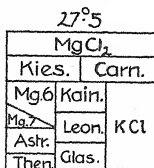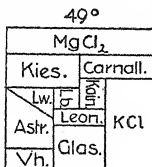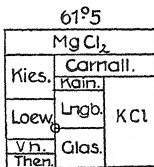
Fig. 41.

While at 25° $MgSO_4, 7H_2O$ appears on the scheme as stable in presence of hexahydrate, kainite, leonite and astrachanite, at 27.5° it is no longer stable in presence of kainite, but only with hexahydrate, leonite and astrachanite. Schönite no longer exists at this temperature, and in its place other double salts appear at higher temperatures, e.g. vanthoffite at 61.5°, which is decomposed at low temperatures.

Magnesium chloride is the last component to crystallise out of the mother liquor.

The general methods given on p. 228 et seq. are useful for preparing the halides of the other bivalent metals; but when a higher halide exists they are most easily obtained by reduction. In particular, those of the chromium group (Cr, Mo, W and the closely related V) and those of the platinum metals are best made in this way. Chromous chloride can be made in the wet way by dissolving the metal in HCl, but usually the chromic salt is reduced with nascent hydrogen (zinc and HCl) or electrolytically, using a lead cathode (W. Traube). All these lower halides are obtained in the dry way by heating the higher halides to their decomposition temperature, either alone (Mo, Pt) or in a current of hydrogen (V, Cr, W). When the metals are heated in a stream of the gaseous halogen acid the hydrogen produced ensures the formation of the lower halide (Fe, Cr). As the bivalent halides sublime at moderate temperatures they can be separated in this way from the metal or the

higher halide, but the temperature must be carefully controlled, as some of the halides have very restricted ranges of stability (cf. the diagram on p. 232). If the decomposition is carried out in a stream of an indifferent gas, e.g. CO_2, it occurs at temperatures below that at which the decomposition pressure is one atmosphere, as the liberated halogen is carried away and the equilibrium disturbed.

The higher halides vary a good deal in ease of decomposition; $MnCl_4$, $PbCl_4$, FeI_3 and CuI_2 decompose at room temperature, PtI_4 at a slightly higher temperature, $PtBr_4$ above 100°, and $PtCl_4$ at the melting point of tin. VCl_4 yields VCl_3 only when its vapour is passed, mixed with hydrogen, through a red-hot tube, and $GeCl_2$ forms a colourless solid when the vapours present after passing $GeCl_4$ over heated germanium are rapidly cooled.[1] $GaCl_2$ is formed by heating $GaCl_3$ with Ga, and $InX_2(X = Cl, Br, I,)$ may be similarly prepared. Titanium trihalides (except the fluoride) when heated *in vacuo* at 400° give tetrahalide, which distils, and the black bihalide :

$$2TiX_3 \longrightarrow TiX_4 + TiX_2.$$
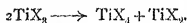
The bihalides are decomposed on further heating to TiX_4 and Ti. $ZrCl_3$ or $ZrBr_3$, formed by reduction of ZrX_4 with metals (250°-500°) in an atmosphere of hydrogen, are similarly converted to ZrX_2, which resemble TiX_2.

Properties.—*The Action of Heat.*—Many of the halides of the bivalent metals give off some of the halogen they contain on heating. The cupric salts yield cuprous salts; the reaction $CuCl_2 \longrightarrow CuCl + Cl$ occurs at a red heat, the bromide is decomposed below a red heat, while the iodide and cyanide both break up at room temperature, the thiocyanate being stable for some time under the latter conditions. When potassium iodide is added to a solution of a cupric salt, cuprous iodide is at once precipitated, and sometimes forms a polyiodide with the liberated iodine. As the reaction takes place in solution and the iodine is soluble, the process is to some extent reversible, $CuI_2 \rightleftharpoons CuI + I$, and if excess of pure CuI is digested with iodine a pale greenish blue solution is obtained containing no free iodine but only cupric salt. Mercuric cyanide gives free metal and cyanogen on heating, with no pause at the univalent stage. The thiocyanate of mercury, $Hg(CNS)_2$, swells in a remarkable manner on heating (Pharaoh's serpents), the products being carbon disulphide and "mellon," $N_3(C_3N_3)_3$.

Those halides which are not decomposed by heat melt at temperatures of several hundred degrees. Many boil without decomposition, the iodides, excepting that of mercury, having the lowest boiling points. Others sublime direct from the solid state; e.g. the dichlorides of Ni, Fe, Mo and V.

[1] Dennis and Hunter, *J. Amer. Chem. Soc.*, 1929, 51, 1151.

The following melting and boiling points are typical :

		Zinc				Tin	
	F	Cl	Br	I	Cl	Br	I
M.pt.	734	262	394	446°	250	215·5	246°
B.pt.	...	730	650°	...	606	619	295°
		Cadmium				Mercury	
M.pt.	520	560	480	404°	277	235	255°
B.pt.	1200	964	860	713°	302	318·5	351°

Allotropy is not a very common phenomenon in this group of halides, but mercuric iodide is an interesting example. It is yellow when precipitated from aqueous solution but rapidly turns red, and when the dry powder is heated it passes into the unstable yellow form at 126°, becoming red again on cooling. The yellow form may be preserved for some time at lower temperatures if, for example, it is made by chilling the vapour; but the reversion is started by scratching or exposure to light and rapidly goes to completion. A third modification is produced when the vapour is cooled under reduced pressure; a colourless powder separates out, but it passes into the red variety in a few seconds. Double halides containing mercuric iodide also show allotropy, but with different transition temperatures; *e.g.* $Cu_2[HgI_4]$, changing from red to black at 71°. Cobalt iodide also exhibits allotropy; the ordinary black anhydrous salt is partly converted into an ochre yellow sublimate when heated *in vacuo*. This substance has the same percentage composition, but dissolves in water to a colourless solution.

Oxidation to the higher halide occurs so readily with the halides of bivalent chromium, vanadium, tungsten and titanium that hydrogen is evolved spontaneously from the acidified aqueous solutions (p. 155), showing that the affinity of these bivalent ions for further positive charges is greater than that of the hydrogen atom. This reaction is so vigorous with the vanadium salt that the dichloride cannot be obtained by the action of acid on the metal, for the trichloride is at once produced. If, however, the vanadous salt is made in the dry way and then dissolved in water, the solution can be kept for some time; it gives off hydrogen continuously, and if a piece of platinum foil is dipped in, the reaction proceeds violently. Colour changes accompany the oxidation—the blue chromous salt and the lavender vanadous salt both turn green. Chromous chloride is one of the strongest inorganic reducing agents, while vanadous chloride bleaches dyes such as litmus and indigo.

Constitution and Molecular Complexity.—Many of the halides of the bivalent metals are normal in molecular weight, both in solution and in the form of vapour. The tendency to polymerise is greater in the tervalent metals; but the vapour density of $SnCl_2$ is slightly high at low temperatures, while compounds of molybdenum are highly polymerised. Like the corresponding compounds of tungsten, niobium and tantalum,

ey are termolecular—Mo_3Cl_6, Mo_3Br_6, Mo_3I_6, as is also indicated by
ieir decomposition products, their slight solubility in water, their
w volatility, and the fact that they are not easily oxidised.
he molecular weight as measured by the rise in boiling point of
iinoline solutions and the lowering of the freezing point of urethane
ilutions is normal. When boiling bismuth chloride is used as solvent
ie results are variable; thus cadmium chloride is normal, whereas
ianganese chloride is termolecular, although it is normal in urethane.
'his is a typical example of the way the complexity varies with the
olvent, and no conclusions can be drawn from these results as to the
:xistence of grouped molecules in the crystalline or fused substance.
iimilarly, changes in grouping usually occur when the substance is
vaporised, and the above results may be explained by compound
iormation with the solvent.

There is thus every indication that some at least of these salts
have two or three molecules conjoined in the crystal state, a structure
which persists even in the ions. The water of crystallisation in
the zinc salts also points to this; in those which have been definitely
characterised — $ZnCl_2,1\cdot5H_2O$ and $ZnCl_2,2\cdot5H_2O$ — the formulae
should at least be doubled, thus: $Zn_2Cl_4,3H_2O$ and $Zn_2Cl_4,5H_2O$.
The most important hydrate of zinc chloride, $ZnCl_2,3H_2O$, should
also have the double formula, thus making it into a hexahydrate,
a form typical of the group. The diamagnetism of gallium dichloride
also suggests the presence of Ga_2Cl_4 in the solid. When the colours of
the uni- and bimolecular salts are different, variations in complexity are
easily seen. Thus, anhydrous cupric chloride is brownish yellow, while
the dilute solution is blue; damp $CuCl_2,2H_2O$ is green, but it turns
brown when concentrated hydrochloric acid is added. The green
colour used to be looked on as a mixture of the brown and the blue,
but solid $CuCl_2,2H_2O$ is blue when quite dry. Kohlschütter[1]
found that when the brown solution of $CuCl_2$ is placed in contact
with one of a colourless chloride and an electric current passed
across the interface, the brown ions move to the anode and copper
is found in the anion. It is therefore very probable that the
solution contains the anion $[CuCl_4]''$ and that the copper chloride
is really the copper salt of this anion, $[CuCl_4]Cu$. On dilution
the complex anions are decomposed into the blue (hydrated) $Cu^{..}$
cation and the Cl' anion: $[CuCl_4]'' \rightleftharpoons Cu^{..}+4Cl'$, and recombine on
concentration or addition of Cl' ions. Probably many of the halides
of this group behave in a similar way, and some have a still greater
tendency to form auto-complexes. The electrical conductivity of cad-
mium iodide shows the same behaviour. The conductivity is remark-
ably small in concentrated solutions (where complex formation is most
pronounced); on dilution, the normal value is rapidly approached

[1] *Ber.*, 1904, **37**, 1160.

owing to the dissociation of the complex. In $N/10$ solution it is only a fifth of that of analogous salts, showing that 80 per cent. of the iodide is undissociated. When an electric circuit is made up of cadmium iodide and an equimolecular solution of cadmium chloride between cadmium electrodes, the E.M.F. developed indicates a ratio of $1 : 3.6$ between the concentrations of Cd$^{..}$ ions in the two solutions; in this instance $[CdI_3]'$ may be the complex ion rather than $[CdI_4]''$. Polymerisation can be detected in zinc iodide, but the property is less pronounced in the bromide and disappears altogether in the chloride. $TlCl_2$ and Tl_2Cl_3 are probably $Tl[TlCl_4]$ and $Tl_3[TlCl_6]$. Mo_3Cl_6 behaves in many reactions as $[Mo_3Cl_4]Cl_2$, for $[Mo_3Cl_4](OH)_2$, $8H_2O$ is obtained by treatment with ammonia; this hydroxide gives salts, $e.g.$ $[Mo_3Cl_4]Br_2$, $3H_2O$, by treatment with acids.

Double Halides.—The auto-complex halides are thus salts in which the same metal appears in both cation and anion: $[CdI_2]_2Cd$; $[CuCl_4]Cu$; naturally, other metals may form the cations of these salts: $[CdI_3]Na$, $[CuCl_4]K_2$. Salts of this kind are known as double halides, since they are formed additively from their components, thus: $CdI_2 + NaI$; $CuCl_2 + 2KCl$. They are very numerous, and include every possible combination.

The *double chlorides, bromides and iodides* of the bivalent metals are as a rule but feeble complexes. On mere recrystallisation from water they are more or less separated into their components (*cf.* carnallite, $KCl.MgCl_2.6H_2O$, p. 237, which is in many respects a typical example of this group of salts). Others are stable in solution, as can be seen by the persistence of the colour of the solid salt. Thus the dark brown colour of concentrated solutions of cupric bromide is changed to a beautiful purplish red when more Br' ions are added (*e.g.* HBr, alkali bromides, and particularly LiBr). The complex salt $Li_2[CuBr_4]6H_2O$ is obtained on evaporation. The corresponding chloride $Li[CuCl_3]2H_2O$ is red in the solid state, but passes through green to blue in solution. $[Co(H_2O)_4]HgCl_4$ is red and $[Mg\{(H_2O)_3\}_4]CoCl_4$ is blue.[1] The potassium salt $K_2CuCl_4.2H_2O$ is less strongly complex and is bluish green in the solid hydrated state, while the anhydrous salt $KCuCl_3$ forms brown needles (the colour of anhydrous $CuCl_2$). Various double halides are known as is shown in the following list of the double bromides of zinc:

Caesium	Potassium	Sodium	Ammonium
...	$KZnBr_3$, $2H_2O$	$NaZnBr_3$, H_2O	$(NH_4)ZnBr_3$, aq.
Cs_2ZnBr_4	K_2ZnBr_4, $2H_2O$	Na_2ZnBr_4, $5H_2O$	$(NH_4)_2ZnBr_4$
Cs_3ZnBr_5	...	...	$(NH_4)_3ZnBr_5$, H_2O

The heavy metals vary considerably in their power of forming double salts; thus cobalt bromide scarcely forms any. The double

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[1] H. Bassett and H. H. Croucher, *J. Chem. Soc.*, 1930, 1784.

fluorides are very stable, and in consequence insoluble metallic fluorides are often more soluble in hydrofluoric acid than in water, with formation of complex acids. An increase in solubility in a solution containing a common ion is usually an indication of the formation of an additive compound, as the presence of a common ion *decreases* the solubility, in the absence of compound formation.

The corresponding *double cyanides* are often more stable complexes and give few ions of the nuclear metal. When solutions of Zn, Ni, Co, Mn, Cd, and especially Fe are treated with potassium cyanide, ill-defined precipitates of the cyanides are first formed; they are amorphous and probably polymerised. These precipitates dissolve easily in excess of the precipitant, thus:

$$Zn(CN)_2 + 2KCN \longrightarrow K_2[Zn(CN)_4]; \quad Fe(CN)_2 + 4KCN \longrightarrow K_4[Fe(CN)_6].$$
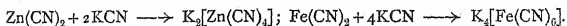
These compounds do not always give the ionic reactions of the heavy metal they contain. Thus $K_4[Fe(CN)_6]$ gives no precipitate of $Fe(OH)_2$ with sodium hydroxide, nor of FeS with ammonium sulphide. Other double cyanides are, however, completely precipitated by ammonium sulphide, as the complex is less stable and some metal ions are present. If enough metal ions are present to exceed the solubility product of the sulphide, if only by a small amount, this quantity will always be formed again when the equilibrium is disturbed by precipitation, until in the end the complex is used up. If, on the other hand, the ionisation into free metal ions does not attain to the solubility product, no separation of sulphide occurs. The reaction is either practically complete or does not occur at all. There is a formal distinction between complex compounds and double compounds, the latter being those which give most of the reactions of their components as their degree of complexity is low, but no sharp limit can be defined, as the two groups merge into one another and the decrease in complexity is gradual.

The complex character is often shown by the colour of the complex salts and ions, which differs from that of the simple salts. Thus $Mn(CN)_2$ dissolved in excess of KCN gives the compound $K_4[Mn(CN)_6]$; the solid compound is a fine dark blue colour, but its solution is only a feeble yellow. Free KCN is present in the solution and, in the air, oxidation of the bivalent manganese proceeds rapidly. The double nickel cyanide $K_2[Ni(CN)_4]$ is a honey yellow solid, but in solution, owing to dissociation of the complex, it is precipitated by $(NH_4)_2S$, though not by NaOH unless bromine or other oxidising agent is present.

The best known and most strongly complex of this group of salts is potassium ferrocyanide $K_4[Fe(CN)_6]$, which, as remarked above, is not decomposed by OH′ ions or by ammonium sulphide. Even acids do not break up the complex, but give the solid white acid $H_4Fe(CN)_6$; this is most easily isolated by the addition of ether to the acid solution of the ferrocyanide, when it is precipitated in combination with two

molecules of ether, which can be removed *in vacuo*. The free acid is rapidly oxidised in the air.

Like the other salts of this class, potassium ferrocyanide is formed when the precipitate of metallic cyanide is dissolved in excess of potassium cyanide. It was formerly manufactured by heating waste nitrogenous animal matter such as scrap horn, leather, or dried blood, with potassium carbonate and iron filings. Air was roughly excluded and the fused mass lixiviated with water. It is now largely prepared from the spent oxide of iron or the cyanogen mud of gas works. These by-products are boiled with milk of lime and the solution of calcium ferrocyanide treated with KCl, when the sparingly soluble $K_2Ca[Fe(CN)_6]$ separates out. This is boiled with K_2CO_3 and thus $K_4[Fe(CN)_6]3H_2O$ is produced.

The salt, which forms large pale yellow crystals, is isomorphous with potassium vanadocyanide $K_4[V(CN)_6]3H_2O$, ruthenocyanide $K_4Ru(CN)_6 . 3H_2O$ and osmocyanide $K_4Os(CN)_6 . 3H_2O$. It is decomposed on heating into nitrogen, potassium cyanide, carbon and iron. In solution it gives, even with very dilute solutions of copper salts, a voluminous precipitate of copper ferrocyanide (a sol is formed if a slight excess of ferrocyanide is present). The general properties of the $[Fe(CN_6)]''''$ complex are discussed with those of the group $[Fe(CN)_6]'''$ on p. 305. Complex ferrous thiocyanates, $M_4[Fe(CNS)_6]xH_2O$, are formed when ferrous chloride acts on alkali thiocyanates in alcoholic solution.

Properties in Solution. — Ionisation — Hydrolysis. — Substances which are highly ionised are not as a rule soluble to any great extent in organic solvents. Those bivalent metal halides which are covalent dissolve in organic solvents, *e.g.* in alcohol, and even in ether, ketones, nitriles and urethane. Only the anhydrous halides dissolve in these solvents, and compounds with the solvent which may be polar, analogous to the salt hydrates, are often formed. The property of dissolving in non-aqueous media is most marked in the feebly dissociated halides of mercury; thus while mercuric chloride is soluble in 15 parts of water at room temperature, it dissolves in 3 parts of ether, and even dissolves to some extent in benzene. The bromide behaves in a similar way, and the iodide, although but slightly soluble in ethyl alcohol, is very soluble in hot amyl alcohol, and to some extent in many other organic solvents. It is remarkable that although the iodide is red these solutions are colourless. This compound also dissolves in liquid ammonia, in pyridine, in sulphur dioxide, and in sulphuryl and thionyl chlorides. In all these solvents it exists as single molecules. The fused mercury salts are considerably ionised and good conductors; on electrolysis the metal separates at the cathode.

The slight ionisation of a salt may be due either to the formation of auto-complexes or merely to the low dissociation of the simple salt.

t is easily seen that in [CuCl$_4$]Cu only half the copper appears as opper ions; but cadmium iodide and the halides of mercury are ven less dissociated. The ionisation of the mercury salts decreases n the order chloride—bromide—thiocyanate—iodide—cyanide, and hat of the cyanide is so low that it no longer gives the usual reactions vith OH′ or I′ ions, although owing to the extremely low solubility)f HgS, a precipitate is formed with H$_2$S. Even with the chloride,)recipitation is often incomplete when equivalent quantities of the former ons are added. The reaction HgCl$_2$+2KOH $\rightleftharpoons$ HgO+2KCl+H$_2$O .s distinctly reversible, as the Hg$^{··}$ ions from HgO tend to form undis-sociated HgCl$_2$, and the less the mercury salt is ionised the more the reaction tends to go to the left. Thus when mercuric oxide is shaken with $N/1$ solutions of potassium halides the following quantities of KOH are liberated:

KCl	KBr	KCNS	KI
0·24	6·36	8·78	76·0 per cent.

For the same reason solutions containing Hg$^{··}$ ions dissolve insoluble chlorides such as silver chloride, by removing Cl′ ions from the solution. Thus in qualitative analysis difficulties arise in testing for silver in presence of Hg$^{··}$ ions; *e.g.* in a solution containing Hg(NO$_3$)$_2$, silver chloride is not precipitated on addition of HCl. Even insoluble mercury salts (*e.g.* the phosphate and arsenate) which can yield Hg$^{··}$ ions to the solution are dissolved by solutions of sodium or potassium chloride. In brief, non-ionised substances tend to be formed from ionic solutions, whether the non-ionised substance is an insoluble precipitate or a soluble substance. Even with hot concentrated sulphuric acid no HCl is evolved from mercuric chloride, since it is necessary for the solubility product of HCl to be exceeded, and not enough Cl′ ions are present to bring this about.

What has been said about the behaviour of mercuric chloride applies with even greater force to the cyanide. Thus free hydrocyanic acid liber-ates HCl from mercuric chloride: 2HCN+HgCl$_2$ $\longrightarrow$ 2HCl+Hg(CN)$_2$, a reaction employed for the alkalimetric determination of HCN.

Mercuric fluoride differs from the other halides of this element in being more strongly ionised in solution; it is also considerably hydro-lysed, and thus approaches more closely to the salts of mercury which do not contain halogens, *e.g.* the sulphate and nitrate. The chloride is hydrolysed slightly—enough to redden litmus but not methyl orange —while the bromide and iodide are still less hydrolysed. The hydrolytic decomposition in the halides of the other bivalent metals can be measured, and in the stannous salts it is so marked that solid basic salts are formed. The salt SnCl$_2$.2H$_2$O dissolves to a clear solution in a little water, but on dilution a precipitate appears which is soluble in acid:

$$SnCl_2 + H_2O \rightleftharpoons Sn(Cl)OH + HCl.$$
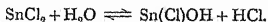
Basic salts are not precipitated from solutions of the other bivalent metals, but hydrolysis can be detected qualitatively by the acid reaction of the solutions, and its extent measured by determining the hydrogen ion concentration in a variety of ways.

Hydrates.—Most of the halides of this group crystallise from water with water of crystallisation. The chief exceptions to this rule are the mercury salts (though the fluoride has two mols. H_2O), cadmium iodide, the slightly soluble lead salts, the insoluble halides of platinum, and finally cupric bromide, which, however, can take up water at very low temperatures. The affinity for water is not very great, for many of these halides, e.g. those of nickel and cupric chloride, become anhydrous on heating on the water-bath; most of them lose their water at temperatures not much above 100°, and only a few, like the magnesium halides, need to be heated above 200° before they become free from water. Most of these salts can be dehydrated without decomposition if carefully heated, but those which require a high temperature frequently give off acid on account of the enhanced hydrolysis, and a basic salt is left behind. This can be avoided by preparing the anhydrous salt by the ignition of the double ammonium halides; thus when NH_4MgCl_3 is heated, pure $MgCl_2$ is left as a residue. If the products of combustion from the burner used for heating come into contact with the salt which is being dehydrated, the water they contain causes hydrolysis, and on prolonged action the halides of multivalent metals are converted into oxides.

The hydration of the amorphous cyanides cannot be stated quantitatively as, like all gelatinous bodies, they contain much adsorbed water. Those that crystallise contain at most four mols. of water, while the slightly soluble fluorides mostly have two mols., only zinc and ferrous fluorides crystallising with four.

The chloride, bromide and iodide of bivalent molybdenum are distinguished from the other bivalent halides by their low water content. The chloride has the formula $MoCl_2 . 1$ or $2H_2O$, or if the persistence of the trimolecular condition in the hydrated state is assumed, $Mo_3Cl_6 . 3$ or $6H_2O$. Cupric chloride also has but two mols. of water of crystallisation. The tin, zinc and cadmium salts, probably owing to polymerisation, are also only slightly hydrated, the first having a maximum of four, the last five mols. of water of crystallisation.

All the other bivalent halogen salts contain six molecules of water of crystallisation in their stable form at ordinary temperatures. When heated, the hexahydrates of iron, manganese, magnesium and chromium halides first give off two molecules of water, and then two more at a higher temperature. The corresponding compounds of nickel and cobalt give the dihydrate in one stage, and the dihydrates often decompose further to give monohydrates. The affinity for water decreases in the series chlorides—bromides—iodides; the iodides are always most easily dehydrated. On the other hand, it is the iodides which contain the greatest quantity of water of crystallisation at low temperatures. Thus even nonohydrates of the iodides of manganese, iron and cobalt, and of the bromide of nickel are known. Magnesium forms hydrates more

easily than any of the other metals of this group; its chloride has as many as twelve, and the iodide and bromide up to ten molecules of water of crystallisation. On heating, the water is lost in groups of two molecules. The capacity for hydrate formation cannot be related to the systematic position of the metals; when the salts are heavily hydrated, like nickel bromide, the water is often given off in stages, each involving two molecules in a short range of temperature, while when the salts are less hydrated the water is more tenaciously held.

There is no direct connection between the deliquescence of a salt and the water content of its hydrates. For instance, a concentrated solution of zinc chloride has a very low vapour pressure—less than the usual partial pressure of water vapour in the air. Solid zinc chloride therefore takes up water from the atmosphere (deliquesces) and can be used as a drying agent for gases. This property does not show, however, that the water is more firmly bound in the crystalline hydrate than in other salts, for many of the salts of this class take up water from an atmosphere saturated with water vapour. This is not described as deliquescence, as saturation of the atmosphere with water vapour is only temporary and local. The difference between zinc chloride and nickel chloride, for instance, is slight and relative. The dehydrated form of even a non-deliquescent salt can often be used with advantage as a drying agent; only the solid hydrate is formed and not a solution, but the rate at which water is taken up is often greater than when a solution is formed. The use of deliquescent substances for drying is due to a prejudice in their favour caused by their appearance.

The determination of the formula of a hydrate by analysis is not always conclusive, owing to efflorescence and the occlusion of mother liquor in the crystals. The composition of the hydrate is better investigated by application of the phase rule. If, for example, a hydrate with 2·1 mols. of water gives the same vapour pressure as the same substance with $6H_2O$, it shows that there is no definite hydrate between these two limits. The existence of a definite hydrate is indicated only when there is a sudden fall in the vapour pressure on decomposition. This is made clear in Fig. 42, which shows the vapour pressures of the hydrates of nickel chloride.

FIG. 42.—Vapour pressure of the hydrates of nickel chloride.

Lescoeur[1] investigated many hydrates in this manner. Inaccuracies arise owing to the formation of solid solutions of one hydrate in another, which makes the decreases in vapour pressure in passing from one hydrate to the other less sudden. If solid solutions are formed to any extent the steps may be quite obliterated, as the phases then consist of a great number of hydrates which differ slightly and continuously in composition, and which are not compounds within the meaning of the law of definite proportions.

Ammines.—The formation of ammines by the addition of ammonia to these halides shows greater regularities than the hydrate formation.

[1] *Ann. Chim. Phys.* and *Compt. rend.*, 1881-1898.

When a stream of dry ammonia is passed over the anhydrous halides they absorb great quantities of the gas, swell up, and finally fall to fine powder. The amminnes can also be obtained in crystalline form from aqueous solution, usually with a lower content of ammonia, as the water not only tends to retain the ammonia itself but also to combine with the salt; organic solvents can sometimes be conveniently employed, e.g. $CoCl_2 . 6NH_3$ is prepared by passing ammonia into an alcoholic solution of $CoCl_2 . 6H_2O$. The ammines, like the hydrates, contain various but definite quantities of the added substance; e.g. nickel chloride forms ammines with 6, 2 and 1 mols. of ammonia, and the decomposition temperature of the ammine with the highest ammonia content shows a remarkable parallelism with the atomic volume of the nuclear metal.[1] The halides of metals of atomic volume lower than 14 (see pp. 36-7) take up 6 mols. of ammonia, while those of metals of greater atomic volume (Hg, Sn, Pb, Ca, Sr, Ba) give no hexammines. Those in which the atomic volume is highest (Ba, Sr, Ca) give ammines of a different class, which decompose readily with liberation of much ammonia and with no pause at the hexammine stage. The following table gives the decomposition

Compound.	Decomposition Temperature.	Compound.	Decomposition Temperature.	Atomic Volume of the Metal.
$NiI_2, 6NH_3$	225·5°	$NiSO_4, 6NH_3$	125°	6·6
$CoI_2, 6NH_3$	188°	$CoSO_4, 6NH_3$	105·5°	6·8
$FeI_2, 6NH_3$	174°	$FeSO_4, 6NH_3$	96°	7·1
$CuI_2, 6NH_3$	115°	$CuSO_4, 5NH_3$	91·5°	7·1
$MnI_2, 6NH_3$	164°	$MnSO_4, 6NH_3$	67°	7·4
$ZnI_2, 6NH_3$	55·5°	$ZnSO_4, 5NH_3$	9°	9·1
$CdI_2, 6NH_3$	97·5°	$CdSO_4, 6NH_3$	60°	12·9
$MgI_2, 6NH_3$	20°	$MgSO_4, 6NH_3$	< −20°	14·0

temperatures of some hexammines at a pressure of 500 mm. of ammonia. Only iodides and sulphates are given, but the chlorides and bromides behave in a similar way to the iodides; some of the sulphates contain only 5 mols. of ammonia as do[2] also $VBr_2 . 5NH_3$ and $VCl_2 . 5NH_3$, which lose ammonia on heating to form $VX_2 . 3NH_3$. The lowering of the decomposition temperature with increase in atomic volume is obvious; only cupric iodide and the cadmium salts lie outside the general sequence.

The colours of the ammines of highest ammonia content are distinctive when the hydrates are also coloured, although the colours are often very different. The nickel salts are a beautiful violet blue, the copper salts sapphire blue, much deeper than the blue of the hydrates. The cobalt compounds are pink, while the manganese and iron ammines are white. The ammines of lower ammonia content

[1] Ephraim, Ber., 1912, 45, 1322.
[2] Ephraim and Ammann, Helv. Chim. Acta, 1933, 16, 1273.

have different colours, those of nickel passing through pale blue and green to brown. The ammines of Ni, Co, Cu, Zn and Cd are soluble in water either alone or on addition of ammonia; a considerable excess of ammonia is necessary for the solution of the cobalt ammines. When the ammines of the salts of magnesium, manganese, bivalent cobalt and iron are dissolved in water, so much free ammonia is formed by the dissociation which occurs that precipitates of the hydroxides are formed. In the other ammines the complex metal-ammine ions persist in aqueous solution, and thus the reaction of the metal with ammonia appears only slightly or not at all. Thus the ammines of the copper salts are not precipitated by addition of a small quantity of sodium hydroxide; indeed, cupric hydroxide is dissolved by ammonia, as the NH_3 molecules combine with the $Cu^{..}$ ions, so that these remain in insufficient quantity to exceed the solubility product of the hydroxide. The complex formed in this instance is not stable enough to resist the action of H_2S, which precipitates the sulphide. Even the hydroxide is precipitated on boiling, for ammonia escapes with the steam, and the complex breaks up to provide the ammonia necessary for the equilibrium. Conversely, excess of ammonia, and even the addition of negative ions, increases the stability of the complexes as required by the law of mass action. The solubility of the ammines is diminished at the same time, and many of them are precipitated from solution on addition of alkali halides and ammonia— particularly the iodide ammines, which are not very soluble. In the air the ammines lose ammonia and usually take up water in its place; this process goes on until all the ammonia is lost, as it diffuses into the air, while the water required for hydration is continuously replaced from the water in the atmosphere. Oxidation also causes the decomposition of ammines containing metals which are susceptible to atmospheric oxidation in presence of hydroxyl ions, e.g. ferrous, manganous, cobaltous and cuprous ammines.

Halides of Tervalent Metals

In these salts it is essential to distinguish clearly between the reactions of the free salts and those of the compounds of the salts with water, ammonia or other halides, as there are often great differences in behaviour between the two classes of substances.

The Anhydrous Halides.—The anhydrous halides of the tervalent metals are produced exclusively in the dry way, since attempts to make them by the dehydration of their hydrates result in hydrolysis, and only basic salts are left. The methods available for the preparation of these substances are therefore:

(1) Treatment of the metal with free halogen; $RuCl_8$ is best obtained from its elements in presence of a trace of CO.

(2) Halogenation of the sulphide or of the oxide in presence of carbon.

(3) Halogenation of the sulphide (p. 229), oxide or sometimes sulphate by S_2Cl_2 and Cl_2, e.g. $4Cr_2O_3 + 9Cl_2 + 3S_2Cl_2 \longrightarrow 8CrCl_3 + 6SO_2$; $2BaSO_4 + Cl_2 + S_2Cl_2 \longrightarrow 2BaCl_2 + 4SO_2$. The former reaction has been applied to the preparation of anhydrous halides of many of the rare earth metals. These can also be made[1] by heating the oxide with ammonium chloride or bromide, followed by removal of the excess of the ammonium halide in vacuo at 300°: $La_2O_3 + 6NH_4Br \longrightarrow 2LaBr_3 + 6NH_3 + 3H_2O$. The excess of ammonium halide prevents hydrolysis by the water formed.

(4) Decomposition of a higher halide either directly or by sulphur (e.g. $VCl_4 \longrightarrow VCl_3 + Cl$ or $NbCl_5 \longrightarrow NbCl_3 + Cl_2$) or by reduction with hydrogen—$UX_4 + H \longrightarrow UX_3 + HX$; $TiCl_4 + H \longrightarrow TiCl_3 + HCl$. Sa, Eu and Yb trihalides are similarly reduced to the bihalides SaX_2, etc. when heated in H_2 or in a mixture of H_2 and NH_3.

(5) The anhydrous chlorides of the cerium earths have been prepared by treating their benzoates with HCl in ethereal solutions.[2]

The colours of the anhydrous halides differ from those of their hydrates. They are summarised in the following table:

	F_3.	Cl_3.	Br_3.	I_3.
Al	White	White	White	White
Fe	Greenish	Violet black flakes, with a greenish sheen	Dark red	Not known
Co	Light brown	Not known	Not known	Not known
Cr	Dark green	Peach blossom red to pale violet shimmering flakes	Dark scales with metallic lustre	Red crystals
Mn	Wine red	Not known		Not known
V	Greenish yellow	Like $CrCl_3$	Grey black	Not known
Ti	Violet	Deep violet shiny scales	Bluish black needles	Black
Au	Not known	Red brown	Brown	Grey green
Bi	White	White	Orange yellow	Shining black, brownish black when precipitated

The chlorides of this group are usually of a violet colour if they are not white; they sublime in scales which usually have a distinctive lustre. The bromides and iodides are darker in colour than the chlorides, while the colour of the fluorides is markedly different from that of the chlorides and approaches that of the hydrated salts. The fluorides also differ from the other salts in having much higher boiling points; these are invariably above 1000°, and the melting points are not much lower. The solid halides have a considerable

[1] Reed, Hopkins and Audrieth, J. Amer. Chem. Soc., 1935, 57, 1159.
[2] Bauman and Takvorian, Compt. rend., 1932, 194, 1579.

vapour pressure and, when heated, sublime without melting; the bismuth compounds and the bromide and iodide of aluminium are exceptional:

	$BiCl_3$	$BiBr_3$	BiI_3	$AlCl_3$	$AlBr_3$	AlI_3
M.pt.	225°	210°	439°	193° (2·5 atm.)	90°	185°
B.pt.	447°	453°	...	183° (sublimes)	265°	>350°

Direct sublimation occurs when the chlorides are heated : of iron at 280°, of chromium at 950°, and of titanium, gold and vanadium at still higher temperatures. Some of them decompose on sublimation, with liberation of free halogen. Thus the vapour of gold chloride gives a pressure of one atmosphere at 256·5°, but this is only a total pressure composed of 0·25 atm. due to $AuCl_3$ and 0·75 atm. due to Cl_2. The bromide gives this pressure at 180°, but with most of these halides the tendency to split off halogen is slight at temperatures just above the boiling point, and is only effective at high temperatures. $CrCl_3$ begins to dissociate at 1200°, $FeCl_3$ at a somewhat lower temperature. The dissociation of MnF_3 into manganous fluoride and free fluorine is one of the few methods of preparing fluorine without the use of electrolysis.

The vapour density of the halides of the tervalent metals is usually in agreement with the simple formula when no dissociation occurs ; this is true not only of $CrCl_3$ at 1200° with its high boiling point, but even of $BiCl_3$ at temperatures just above its much lower boiling point. On the other hand, $AlCl_3$, AlI_3, $GaCl_3$ and $FeCl_3$ show a double molecular formula at lower temperatures, and $CrCl_3$ would probably do the same if it were possible to obtain its vapour at low temperatures. The double formula of these halides can be observed at temperatures below 440°, and with rise in temperature gradual dissociation into single molecules occurs and is complete at 660° for $AlCl_3$ and at 750° for $FeCl_3$.

Many of these halides are soluble in organic solvents, and in solution the simple molecular weight is often retained, e.g. $FeCl_3$ in ether and $AlCl_3$ in pyridine. When $AlBr_3$ is dissolved in carbon disulphide, however, it shows the double molecular weight, as does $Fe[Fe(CNS)_6]$ in ether or benzene. The dipole moment of liquid aluminium bromide and of its solutions in bromine, carbon disulphide or benzene is zero, thus confirming the doubled formula.

The tendency for a solvent to depolymerise substances dissolved in it is related to the dielectric constant.[1] This indicates that electrical forces operate in depolymerisation just as they do when ions combine to form a neutral molecule, a process which also depends on the dielectric constant of the medium. The polymerised halides were formerly given formulae like $Cl_3Al . AlCl_3$, in which chain formation similar to that which takes place in organic compounds was assumed. But there is no indication that the valency of the metal has undergone any fundamental change, and it is simpler to assume that the affinity of each Cl atom is distributed between two Al atoms, so that each metal atom retains six half-atoms of chlorine, as indicated

---

[1] Walden, Z. Elektrochem., 1920, 26, 60.

by the formulation [Al{Cl$_6$}Al]. As will shortly be explained, the combination of the metal atom with six acid radicals is very common; in this instance the polymer is the aluminium salt of the complex acid [AlCl$_6$]H$_3$.

The electronic formula

$$\text{Cl}^6 \quad \overset{+}{\text{Cl}^4} \quad \overset{-}{\text{Al}} \quad \text{Cl}^6 \qquad i.e. \qquad \text{Cl} \quad \text{Al} \quad \text{Cl} \quad \text{Al} \quad \text{Cl}$$
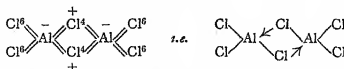
and similarly for Fe$_2$Cl$_6$ are in accordance with the observed molecular complexity.

AuBr$_3$ is dimeric in boiling bromine [1] leading to the formulation :

$$\text{Br} \quad \text{Au} \quad \text{Br} \quad \text{Au} \quad \text{Br}$$
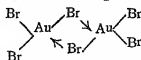
These compounds show a fairly marked solubility in organic solvents; some are soluble in ether and in pyridine, etc., probably forming compounds with the solvent. Compounds of VCl$_3$ with benzene and with ether (blue), and of BiBr$_3$ with ether, have been isolated. The compounds with amines will be discussed in greater detail later on. The solubility of these acid halides in non-ionised halogen compounds is remarkable; thus AuCl$_3$ is soluble in SbCl$_3$, AsCl$_3$ and SnCl$_4$, and can be recrystallised from these solvents. Double halides are frequently formed with halides of the non-metals. Aluminium chloride is particularly prone to form such compounds, and even combines additively with the most unlikely substances, e.g. :

NO, NO$_2$, PH$_3$, PCl$_3$, POCl$_3$, H$_2$S, SCl$_4$, SeCl$_4$, S$_2$Cl$_2$, SOCl$_2$, SO$_2$, NOCl, NH$_3$, etc.
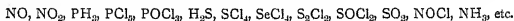
Many of these can be distilled unchanged, and possibly contain aluminium of co-ordination number 4, e.g. Cl$_3$Al ←— PH$_3$.

The effect of water on the tervalent metal halides is very variable. When the fluorides have been prepared in the dry way, they are remarkably insoluble in water, and resist even boiling sulphuric acid or alkalis; at most they dissolve slightly in hydrofluoric acid with formation of complex fluorides. On the other hand, the precipitated metallic hydroxides dissolve easily in aqueous hydrofluoric acid, with no tendency to reprecipitate the fluoride. Bismuth fluoride alone comes out of solution on dilution. When solutions of the fluorides are evaporated, hydrates are left which have different properties from those of the anhydrous salts.

The chlorides show all the stages in the reaction of these halides with water. Some hydrate readily; the halides of aluminium dissolve in water with a hissing sound and with great evolution of heat. These deliquesce in moist air very rapidly and with development of fumes, for hydrolysis occurs at the same time as hydration, and the HCl produced is less soluble in the concentrated solution than in water; conversely, AlCl$_3$.6H$_2$O is precipitated from aqueous solution by saturating

[1] Burawoy and Gibson, *J. Chem. Soc.*, 1935, 217.

with HCl gas (see p. 233).   Ferric chloride, bismuth chloride and vanadium trichloride are all hygroscopic, but less so than the aluminium salt.   On the other hand, $CrCl_3$ and $TiCl_3$ have the striking property of remaining for a long time in contact with cold water without reacting or dissolving.   Apparently they are not wetted by the water and are thus preserved from its action.   Hydration is catalysed by substances which may either have a chemical action or alter the surface tension of the water-salt surface.   Thus if a very small quantity of $CrCl_2$ or $TiCl_2$ is added, the anhydrous chloride dissolves at once.   Even the contact of metallic tin is sufficient to give enough chromous salt to start the hydration.

No anhydrous cyanides of this group are known, and of the thio-cyanates only that of bismuth is known as a yellow solid, soluble in water.

Hydrates and Complex Compounds

Hydration.—The chlorides, bromides and iodides of this group crystallise as a rule with a maximum of $6H_2O$; only the bismuth salts combine with smaller quantities of water—the chloride with $2H_2O$, the other halides being anhydrous.   Higher hydrates are formed as follows :

$$CrI_3 . 9H_2O \qquad AlBr_3 . 15H_2O \qquad AlI_3 . 15H_2O,$$
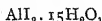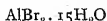
but they are decomposed at very low temperatures.   The fluorides usually crystallise with less water than the other halides of this group ;

FIG. 43.—Hydrates of ferric chloride.

for example, that of manganese crystallises with 3, that of iron with 4·5 molecules of water.   Roozeboom[1] studied the hydrates of ferric chloride in great detail.   His work gives an idea of the methods used in finding lower hydrates of this kind of compound, and is also of historical interest as being one of the first applications of the method of thermal analysis (see p. 865) to the detection of salt hydrates.   He examined the freezing points of all the possible mixtures of $FeCl_3$ and H_2O.
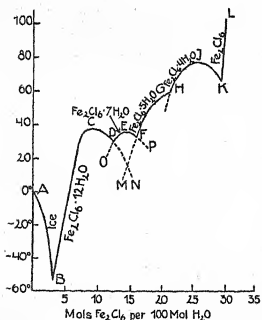
At A in Fig. 43, with a hundred molecules of H_2O and 0 mol. $FeCl_3$, the freezing point is 0°—that of pure water.   On addition of a little $FeCl_3$ the freezing point falls rapidly towards B, and as on freezing between A and B only ice crystallises out, the mother liquor becomes richer in $FeCl_3$.   On cooling solutions of composition between B and C, the hydrate $Fe_2Cl_6 . 12H_2O$ separates out and the solution becomes weaker

[1] *Z. physikal. Chem.*, 1892, 10, 447.

in $FeCl_2$. At B, however, the solution freezes as a whole, ice and the hydrate crystallising out together, so that B is a eutectic point. The liquid also freezes uniformly at C, giving pure crystals of $Fe_2Cl_6 . 12H_2O$. C is thus the maximum point which is always obtained when the composition of the liquid is that of a definite compound. The composition of the solid is the same as that of the liquid, both at maximum points and at eutectic points, but along the curves that lead to them compounds crystallise out which differ in composition from the mother liquor. The composition of the liquid is thus altered and tends to approach the nearest eutectic, and when that is reached it freezes as a whole at a definite temperature.

The normal freezing-point curve of $FeCl_3$–H_2O mixtures is the continuous curve ABCDEFGHJKL, but owing to supersaturation unstable conditions arise. In particular, the section DEF is often missed in following the curves from C and G, as D and F pass unnoticed and only the intersection at N is found. The point N also represents an unstable condition, and by appropriate treatment the compound E and some mother liquor is recorded as shown on the branch PEO. It is notable that the compound E has a lower freezing point than the hydrate C, which contains more water. The composition of the hydrates indicates that the $FeCl_3$ is present in the bimolecular form.

The melting points of the hydrates and eutectics are as follows :

Hydrates.			Eutectics.		
Point.	Hydrate.	Melting Point.	Point.	Eutectic.	Melting Point.
C	$Fe_2Cl_6 . 12H_2O$	37°	B	Ice–$Fe_2Cl_6 . 12H_2O$	ca. $-55°$
E	„ $7H_2O$	32·5°	D	$Fe_2Cl_6 . 12H_2O$–„ $7H_2O$	27·4°
G	„ $5H_2O$	56°	F	„ $7H_2O$–„ $5H_2O$	30°
J	„ $4H_2O$	73·5°	N	„ $12H_2O$–„ $5H_2O$	ca. 15° (unstable)
			H	„ $5H_2O$–„ $4H_2O$	55°
			K	„ $4H_2O$–Fe_2Cl_6	66°

Special Properties of the Manganese Salts.—It is remarkable that manganese trifluoride is the most stable in solution of all the salts of tervalent manganese, though $NH_4H_2Mn^{III}(PO_4)_2$ has been prepared and the tartrates are also stable. When the higher oxides of manganese are dissolved in hydrofluoric acid the fluoride crystallises from the dark red solution as ruby crystals ; it is also produced in the form of double salts when manganous salts are treated with permanganate in HF solution. Ordinarily the action of permanganate on manganous salts produces a precipitate of $Mn(OH)_4$, but in all probability a manganic salt is always first formed, which is unstable except as a weakly dissociated or complex fluoride. The decomposition of the manganic salts is best studied in the chloride, which is not so stable as the fluoride, but which can be obtained if the concentration of $Mn^{...}$ ions is kept low by the formation of complexes. The reversible reaction $2Mn^{...} + 2Cl' \rightleftharpoons 2Mn^{..} + Cl_2$, which normally goes fairly completely from left to right, can then be made to go to some extent in the opposite direction. The tendency for compounds of tervalent Mn to form compounds of bi- and quadri-valent manganese spontaneously—

$2Mn^{\cdots} \longrightarrow Mn^{\cdots} + Mn^{\cdots\cdots}$—also makes the preservation of $Mn^{\cdots}$ more difficult. The $Mn^{\cdots\cdots}$ compounds hydrolyse readily, with formation of insoluble $Mn(OH)_4$, and thus the tervalent compound is rapidly used up. When this hydrolysis is repressed by excess of acid, and advantage is taken of the ease with which double halides of $Mn^{\cdots}$ with the alkali metals crystallise out, it can be shown that $Mn^{\cdots}$ is present as well as $Mn^{\cdots\cdots}$ and $Mn^{\cdot\cdot}$, even when the solution of the higher manganese chloride is derived from quadrivalent manganese (Meyer and Best).

Hydrolysis.—The electropositive character of metals decreases with increase in valency, and in consequence the tendency of the salts to hydrolyse increases. Hydrolysis is an outstanding property of the halides of the tervalent metals, and in the cyanides it is sometimes so pronounced that they cannot be formed at all (*e.g.* Al), HCN being such a weak acid. Only when the cyanides give complexes can they be kept as such. The fluorides and thiocyanates are also much hydrolysed, and hence find application as mordants in dyeing when it is desired to precipitate the hydroxide on the fabric. The hydrolysis of the chlorides is less complete, but bismuth and antimony trichloride decompose completely owing to formation of the insoluble crystalline basic salts, *e.g.*: $BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$. The hydrolysis of the other chlorides is not visible in the cold, but can be seen when the solutions are heated to high temperatures under pressure. The basic salts or hydroxides formed in this way do not redissolve on cooling, even on addition of more acid, as they are changed into less soluble forms (see p. 456). The extent of hydrolysis has been measured, *e.g.* for aluminium chloride: a $N/1024$ solution is hydrolysed 4·5 per cent. at room temperature and has a distinctly acid reaction, while at 99° even a $N/512$ solution is hydrolysed 41·4 per cent. At higher temperatures the insoluble hydroxide is formed, and even at room temperature a solution of the hydroxide can be formed by dialysing the chloride solution.

Constitution and Isomerism.—The solutions of these salts if not colourless have colours different from those of the anhydrous salts. Ferric and auric chlorides are yellow to brown, but the others have two distinct colours—green and violet (Cr, Mn, V, Ti). The isomeric green and violet forms occur also in the double halides of these elements, and are due to differences in the way the chlorine and water are linked to the metal atom. The chromium compounds have been studied in most detail, and are considered in the next chapter (p. 292).

THE CO-ORDINATION THEORY
AND THE AMMINES

Complex compounds—The co-ordination theory—The field valency theory—Double halides of tervalent metals—Cobaltammines and chromammines—Multinucleate ammines.

Werner's Co-ordination Theory

IT is remarkable that the sum of the halogen atoms and the water molecules in many double halides is *six*. Take, for example, the double vanadium fluorides:

$$\left[V \begin{matrix} F_3 \\ (H_2O)_3 \end{matrix} \right] \qquad \left[V \begin{matrix} F_4 \\ (H_2O)_2 \end{matrix} \right] NH_4 \qquad \left[V \begin{matrix} F_5 \\ (H_2O) \end{matrix} \right] (NH_4)_2 \qquad \left[VF_6 \right] (NH_4)_3$$

$$VF_3, 3H_2O \qquad NH_4F, VF_3, 2H_2O \qquad 2NH_4F, VF_3, H_2O \qquad 3NH_4F, VF_3.$$
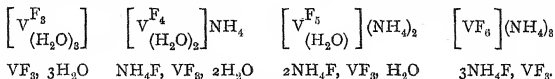
According to Werner's theory the halogen atoms and the water molecules form a complex with the metal atom, in which six components can be attached to the latter. The theory is supported not only by the examples given here but by many others. This can be seen by a consideration of the empirical formulae as shown below.

Complex Compounds — Werner pointed out the analogy between the double halides and the salts of the oxyacids. When water is added to an acidic oxide an acid is formed and a similar reaction takes place when hydrochloric acid is added to a chloride:

$$SO_3 + OH_2 = [SO_4]H_2 \qquad SbCl_5 + ClH = [SbCl_6]H,$$

and, similarly, whereas oxides of metals combine with oxides of non-metals to give oxysalts, metallic chlorides combine with chlorides of less positive metals to give double chlorides (chlorosalts) ·

$$SO_3 + OK_2 = [SO_4]K_2 \qquad AuCl_3 + ClK = [AuCl_4]K.$$

On the other hand, hydrochloric acid reacts with oxides in the same way as chlorides react with water:

$$SO_3 + HCl = [SO_3Cl]H \qquad AuCl_3 + H_2O = [AuCl_3O]H_2.$$

The analogy is far from being merely superficial, for the properties of the addition products are similar. An acid is formed both by the addition of water and by that of hydrochloric acid, and the hydrogen in

consequence is ionised in both types of compounds. This is shown in the above formulae, where the hydrogen is placed outside the square brackets, the whole of the atoms inside the brackets forming the other ion, thus:

$$\left[SO_4\right]'' \qquad \left[S{}^{O_3}_{Cl}\right]' \qquad \left[Au{}^{Cl_3}_{O}\right]'' \qquad \left[AuCl_4\right]'.$$
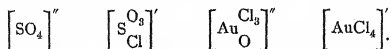
These ions, which contain either chlorine or oxygen, or both, do not differ in their negative character or in their capacity to form salts. The ions $[AuCl_4]'$ and $[SO_3Cl]'$ are univalent, while the others are bivalent, but this is merely due to the fact that only one mol. of HCl has been added in this instance, and in other compounds where two mols. of HCl or one molecule of water are added the ion is bivalent: $PtCl_4 + 2HCl = [PtCl_6]H_2$.*

Compounds like these are described as complex compounds. They may contain components which are themselves capable of separate existence. Thus SO_3, $SbCl_5$, H_2O, HCl, $AuCl_3$ and KCl can all exist separately, and when combined they form complex compounds. The components of a complex compound are sometimes very firmly combined; sometimes the forces which hold them together are fairly weak.

Complex compounds are very numerous. They include the salt hydrates, e.g. $MgCl_2$, $6H_2O$ (for $MgCl_2$ and H_2O can exist separately), the ammines of salts, such as $AgCl$. $3NH_3$, double salts like K_2PtCl_6 i.e. $2KCl + PtCl_4$, $K_3Co(NO_2)_6$ i.e. $3KNO_2 + Co(NO_2)_3$, and many other classes of compounds, which will be considered in their turn. It often happens that the complex is more stable than its separate components. Thus K_2MnCl_6 ($= 2KCl + MnCl_4$) is stable, whereas $MnCl_4$ cannot be isolated. It would therefore be more accurate to define complex compounds as substances formed by the combination of components which are already saturated according to the classical concepts of valency.

The analogy between the addition products of $PtCl_4$ and water or HCl is very complete. The chloride can take up two mols. of HCl or two of H_2O or even one of each at the same time. In all these cases a dibasic acid is formed, for the Cl of the HCl or the OH of the H_2O becomes attached to the $PtCl_4$ in a way which does not permit it to dissociate, thus:

$$PtCl_4 + 2HCl \qquad PtCl_4 + HCl + H_2O \qquad PtCl_4 + 2H_2O$$

$$\left[PtCl_6\right]H_2 \qquad \left[Pt{}^{Cl_5}_{OH}\right]H_2 \qquad \left[Pt{}^{Cl_4}_{(OH)_2}\right]H_2.$$
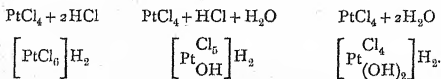
While the total number of Cl and OH groups attached to the platinum atom is invariably six, the two components can be inter-

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* Some halides of quadrivalent elements will be introduced into this discussion to make it more complete.

changed indiscriminately without altering the general character of the compound. Miolati[1] (see also p. 329) was able to continue the series further, partly by preparing new compounds and partly by placing known ones :

$$\left[Pt\begin{matrix}Cl_2\\(OH)_4\end{matrix}\right]H_2 \qquad \left[Pt\begin{matrix}Cl\\(OH)_5\end{matrix}\right]H_2 \qquad \left[Pt(OH)_6\right]H_2.$$
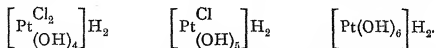
There is thus a complete transition between $[PtCl_6]H_2$ and $[Pt(OH)_6]H_2$ by replacement of each Cl atom successively by OH. The middle member of the series $\left[Pt\begin{matrix}Cl_3\\(OH)_3\end{matrix}\right]H_2$ has not, indeed, been prepared, but compounds of similar composition are well known. Analogous complexes can be obtained from the bromides and iodides, and the halogen atoms in all of them can be replaced by OH groups or by atoms of other halogens, without altering the electro-chemical properties of the complex radical: all these compounds are dibasic acids, and Cl, Br, I and OH replace one another equivalently.

Substitution is not always without effect on the behaviour of the complex, as may be seen by comparing the above series with that of the double vanadium fluorides on p. 279. In the latter the halogen is also replaced atom by atom by H_2O, but the H_2O is not electrically equivalent to the fluorine, and, in consequence, the valency of the complex is reduced by unity at each replacement. Compounds in which the halogen atoms are replaced by NH_3 are more numerous and better known than these double fluorides. The ammonia behaves in the same way as the water in the above example. The following series is a good example of this :

$$\left[Co(NH_3)_6\right]^{\cdots} \qquad \left[Co\begin{matrix}(NH_3)_5\\Cl\end{matrix}\right]^{\cdots} \qquad \left[Co\begin{matrix}(NH_3)_4\\Cl_2\end{matrix}\right]^{\cdot} \qquad \left[Co\begin{matrix}(NH_3)_3\\Cl_3\end{matrix}\right]$$
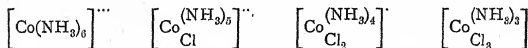
The first complex is a tervalent cation. The entry of each chlorine atom causes a reduction in valency of one unit, so that the last in the series, after three chlorine atoms have replaced as many mols. of ammonia, has zero valency. It is no longer an ion, but an electrically neutral compound, which does not combine with other ions to form salts. The conductivity of these compounds decreases with the introduction of chlorine and is reduced to zero in the last member of the series. As an example, the conductivities of a series of chlorides in which the NH_3 group is replaced step by step by the nitrite group are given for $N/500$ solutions :

$$\left[Co(NH_3)_6\right]Cl_3 \qquad \left[Co\begin{matrix}(NH_3)_5\\NO_2\end{matrix}\right]Cl_2 \qquad \left[Co\begin{matrix}(NH_3)_4\\(NO_2)_2\end{matrix}\right]Cl \qquad \left[Co\begin{matrix}(NH_3)_3\\(NO_2)_3\end{matrix}\right]$$

$\mu =$ 412   240   97   1·5

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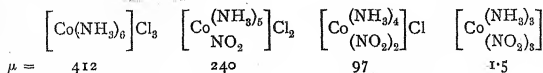
[1] *Z. anorg. Chem.*, 1900, **22**, 445.

and they are arranged in a symmetrical fashion at the corners of an octahedron. Werner has shown that this arrangement is extremely likely from a consideration of the behaviour of the isomers of these compounds.

A brilliant proof of the octahedral arrangement of the groups was brought forward as a result of the X-ray analysis of the crystals.[1] It has been shown that compounds like $[Ni(NH_3)_6]Cl_2$, $Rb_2[PdBr_6]$, $(NH_4)_2[SiF_6]$, $[Co(NH_3)_6]Cl_3$ all have the same crystal structure; the ammonia molecules or halogen atoms in the square brackets are arranged at the corners of an octahedron surrounding the central atom. In fact, the salts have the same crystal lattice as fluorspar (p. 258), the bracketed complexes being in the positions occupied by the Ca atoms. The dimensions of the crystal units were determined, and it was shown that the atoms which form the simple ions are farther away from the central atom than the units in the complex.

Co-ordination and Electronic Theory of Valency.—Sidgwick[2] assumed that two electrons were present in each co-ordination bond of such compounds and in many cases the total electron shells of inert gases are thereby attained:

Element.	Atomic Number.	Electrons lost in Ion Formation.	Electrons gained in Co-ordination.	Total Shell.
Fe(ous) . .	26	2	12	36
Co(ic) . .	27	3	12	36
Cu(ous) . .	29	1	8	36
Zn . . .	30	2	8	36
Mo . . .	42	4	16	54
Pd . . .	46	4	12	54
Ir . . .	77	3	12	86
Pt . . .	78	4	12	86

In other elements which form complexes—often very stable ones—the total number of electrons may either not attain or may even exceed the number in the inert gas shell, for example:

Element.	Atomic Number.	Electrons lost in Ion Formation.	Electrons gained in Co-ordination.	Total Shell.
Cr . . .	24	3	12	33
Fe(ic) . .	26	3	12	35
Co(ous) . .	27	2	12	37
Ni . . .	28	2	12	38
Cu(ic) . .	29	2	8	35
Zn . . .	30	2	12	40

The tendency is not, therefore, merely to attain the inert gas structure, although this appears to be significant: it is also necessary

[1] Scherrer and Stoll, *Z. anorg. Chem.*, 1922, 121, 319; Wyckoff and collaborators, *J. Amer. Chem. Soc.*, 1921, 43, 2292; 1922, 44, 1239, etc.
[2] *J. Chem. Soc.*, 1923, 123, 725; 1941, 433.

to produce a symmetrical structure (planar, tetrahedral, octahedral or cubic) irrespective of the actual number of electrons involved.

In order to consider more precisely the nature of the bonds present, the group $[Co(NH_3)_6]$ may be written, using the Main Smith notation, as follows :

$$NH_3$$
$$NH_3 \underset{Co}{\overset{|}{\Big|}} NH_3$$
$$NH_3 \diagup\!\!\!\diagdown NH_3$$
$$H = N = H$$
$$\overset{\|}{H}$$
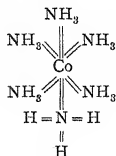
one NH_3 being written more fully than the others to assist in the summation of charges. When the charges on each atom are summed as described on p. 51 the following results are obtained :

	H	N	Co
Charges due to shared electrons	-1	-4	-6
Charges due to unshared electrons	0	0	0
Core charge	$+1$	$+5$	$+3$
Resultant charge	0	$+1$	-3

The grouping is, therefore, as below (II), carrying a resultant charge of $+6-3 = +3$. Each NH_3 group may be considered to combine with the cobalt ion by virtue of its lone pair of electrons and the grouping may accordingly be written as in (III) below :
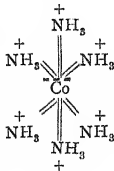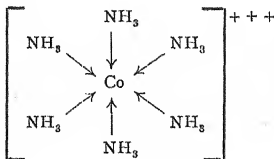
II. III.

This type of bonding—the semi-polar bond (Sugden) or the co-ordinate link (Sidgwick)—is common in practically all such compounds containing groups capable of independent existence, i.e. it may in a sense be regarded as a subspecies of covalent link.

In the same way $[CoCl_6]$ may be written as in (IV) and (V) :
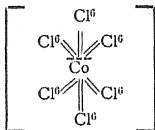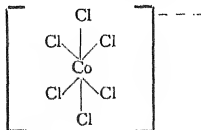
IV. V.

the chlorine atoms being linked by true covalencies, the Co atoms having gained three electrons from the metal ions with which the group combines (*e.g.* K_3CoCl_6).

The intermediate types, containing both ammonia and chlorine, all fit in with these views, *e.g.*:—

carrying a resultant charge of $5 - 3 = +2$
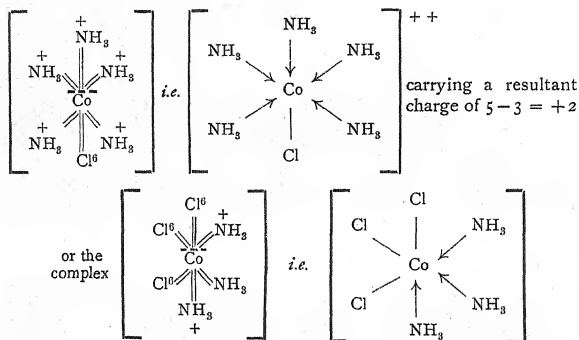
The representation of other co-ordinating elements and groupings is analogous, provided due account is taken of the particular factors of each case, such as the valency of the central atom. Thus as the core charge of quadrivalent Pt is $+4$, $[Pt(NH_3)_4Cl_2]Cl_2$ would be written
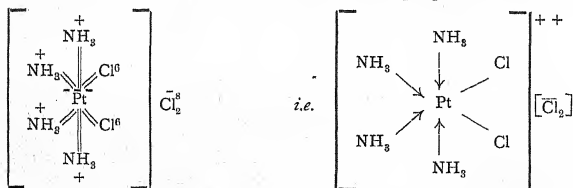
and the bivalent platinum compound $[Pt(NH_3)_4]Cl_2$ is
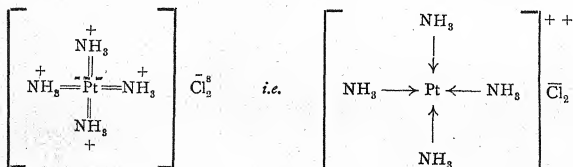
Sudgen[1] considered that in such compounds the octet rule should not be abandoned and that valency shells larger than the outermost group of eight in inert gases should not be presupposed. He therefore formulated such compounds with single electron links, and considered that such representation gave a more plausible distribution of electronic charges, *e.g.* Co in $[Co(NH_3)_6]Cl_3$ is not shown as negative relative to N.

His formulations, using the Main Smith notation, are indicated in the following examples:

$$\left[\begin{array}{c} +\tfrac{1}{2}\overset{1}{NH_3} \\ +\tfrac{1}{2}\overset{1}{NH_3}\diagdown \big| +\tfrac{1}{2}\overset{1}{NH_3} \\ Co \\ +\tfrac{1}{2}\overset{1}{NH_3}\diagup \diagdown +\tfrac{1}{2}\overset{1}{NH_3} \\ +\tfrac{1}{2}\overset{1}{NH_3} \end{array} \right] \qquad \left[\begin{array}{c} -\tfrac{1}{2}\overset{7}{Cl} \\ -\tfrac{1}{2}\overset{7}{Cl}\diagdown \big| -\tfrac{1}{2}\overset{7}{Cl} \\ Pt+ \\ -\tfrac{1}{2}\overset{7}{Cl}\diagup \diagdown -\tfrac{1}{2}\overset{7}{Cl} \\ -\tfrac{1}{2}\overset{7}{Cl} \end{array} \right]$$
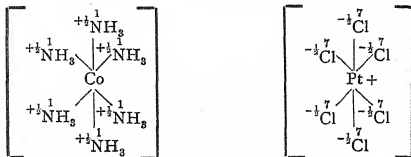
the first grouping carrying three positive charges and the second two negative charges.

These views find their counterpart in his formulations of PCl_5 $SbCl_5$, etc. (p. 53), but have met with no general acceptance; single electron linkages are probably present only in exceptional cases and not in stable compounds of these types.

As was shown on p. 56, the modern view of complex compounds involves the hybridisation of the bond orbitals of the central atom to give, in the case of cobalt, six equivalent bond orbitals, each joining covalent bonds of greater strength than any of the pure bond orbitals from which they spring. Moreover, this treatment of the cobalt complex leads to the establishment of the six bonds directed towards the corners of a *regular* octahedron, whilst the experimental data which arose from Werner's theory, can only establish an octahedron, without providing any information as to its regularity or otherwise. The mathematical difficulties involved in the quantum-mechanical consideration of complexes preclude an immediate extension to all the complexes known, but it may be assumed that in general orbital hybridisation occurs, resulting in the formation of the strongest possible bonds and a definite configuration.

Co-ordination Valency of the Radical.—The effect of replacing the NH_3 groups by amines which contain two NH_2 groups is of interest. Ethylenediamine, $NH_2.CH_2.CH_2.NH_2$, indicated by (en), and propylenediamine, $NH_2.CH_2.CH_2.CH_2.NH_2$, indicated by (pn), each replace two NH_3 molecules, thus:

$$[Co(NH_3)_6]Cl_3 \quad \text{and} \quad [Co(en)_3]Cl_3 \quad \text{or} \quad [Co(pn)_3]Cl_3;$$

$$\left[Co\begin{array}{c}(NH_3)_4 \\ Br_2\end{array}\right]I \qquad \text{and} \qquad \left[Co\begin{array}{c}(en)_2 \\ Br_2\end{array}\right]I.$$
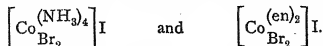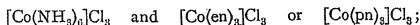
Whereas H_2O and NH_3 each occupy but one of the co-ordination

[1] *The Parachor and Valency*, London, 1930, p. 141.

positions, the (en) and (pn) molecules each occupy two. Groups which occupy two co-ordination positions, and in some cases even three or four positions, are termed *chelate*[1] (= a crab's claw) groups.

Although water is equivalent to NH_3 in utilising only one of the co-ordination positions, substances which have several hydroxyl groups frequently occupy two co-ordination positions per molecule. Glycol, $HO.CH_2.CH_2.OH$, for instance, gives the ion $[M(glycol)_3]$ corresponding to the ion $[M(H_2O)_6]$. These types, formed with ethylenediamine, glycol, glycine and oxalic acid may be formulated:

$$\left[M \left\langle \begin{array}{l} NH_2-CH_2 \\ | \\ NH_2-CH_2 \end{array} \right\rangle_3 \right], \quad \left[M \left\langle \begin{array}{l} H \\ O-CH_2 \\ | \\ O-CH_2 \\ H \end{array} \right\rangle_3 \right],$$

$$\left[M \left\langle \begin{array}{l} NH_2-CH_2 \\ | \\ O-CO \end{array} \right\rangle_3 \right], \quad \left[M \left\langle \begin{array}{l} O \quad CO \\ | \\ O \cdot CO \end{array} \right\rangle_3 \right]$$
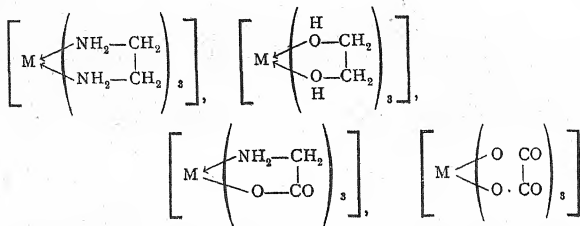
They afford examples of the various types of bidentate groups which may be met with, as in $\alpha\alpha'$-dipyridyl ferrous sulphate.
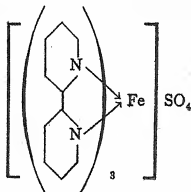
nickel salicylaldoxime
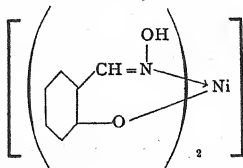
and potassium aluminium oxalate $K_3 \left[Al \left\langle \begin{array}{l} O \cdot CO \\ | \\ O \cdot CO \end{array} \right\rangle_3 \right]$
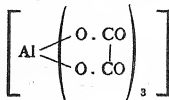
Glycerol, although it has three hydroxyl groups, only takes up

[1] Morgan and Drew, *J. Chem. Soc.*, 1920, 117, 1457.

two co-ordination positions, as might be expected from steric considerations, but α-β-γ-triaminopropane[1] behaves as a tridentate group in

$$\left[\begin{array}{c} CH_2 \cdot NH_2 \\ CH_2 \cdot NH_2 \longrightarrow Rh \longleftarrow NH_2 \cdot CH_2 \\ CH_2 \cdot NH_2 \end{array}\right] Cl_3$$

Chloro-tripyridyl platinous chloride,[2]

$$\left[\text{structure}\right] Cl, 2 \text{ or } 3H_2O$$
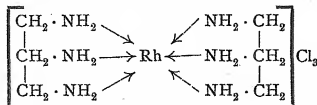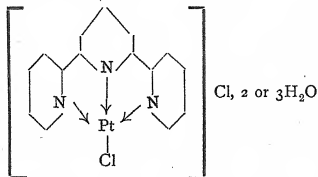
is an interesting tridentate type; the rings can only be strainless if the four attached groups are co-planar with the platinum (see p. 348). Similar compounds are known with the following central atoms:— Cu^{++}, Ag^{++}, Zn^{++}, Cd^{++}, Hg^{++}, or Pd^{++}, and the chloride ion may be replaced by other univalent anions.

The radicals of polybasic acids often occupy several co-ordination positions. Thus the derivative of the Cl^I ion (I) is equivalent to that of the SO_4^{II} ion (II) and to that of the oxalate ion (III), thus:

I.

II.

III.
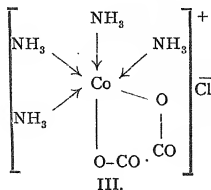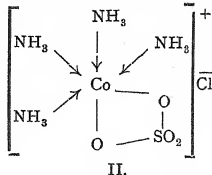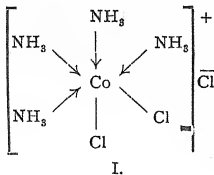
[1] Mann and Pope, *Proc. Roy. Soc.*, 1925, **107A**, 80 ; *J. Chem. Soc.*, 1926, 2675.
[2] Morgan and Burstall, *J. Chem. Soc.*, 1934, 1498.

Sometimes the ion of a polybasic acid occupies only one position as in:

$$\left[Co\begin{matrix}(NH_3)_5 \\ SO_4\end{matrix} \right]Cl,$$
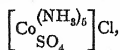
which, like (II), forms a univalent complex ion. This can be formulated as

$$\left[Co\begin{matrix}(NH_3)_5 \\ O\end{matrix} \right]^{++} \!\!\!\!\!\!\!\!\!\!\!\! -SO_2-\bar{O},$$
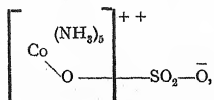
the sulphate group being partly within and partly without the complex. Similarly, $Na[P_2O_7Co(NH_3)_5]$ with the tetrabasic pyrophosphate radical occupying only one co-ordination position can be regarded as
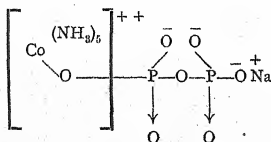
Further, chelate groups such as ethylenediamine may sometimes occupy only one co-ordination position; for example $[Pt^{II}en_2]Cl_2$ yields a dihydrochloride with hydrochloric acid which with K_2PtCl_4 followed by NaOH gives a red platinochloride. These reactions are formulated thus[1]:
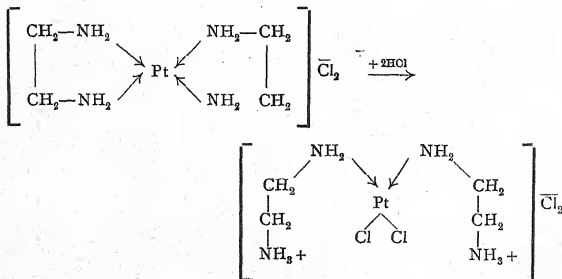
[1] Drew and Smith, *J. Chem. Soc.*, 1936, 1067; Drew, *ibid.*, 1932, 2328; Drew and Tress, *ibid.*, 1933, 1335.

$$\xrightarrow{\text{K}_2\text{PtCl}_4} \begin{bmatrix} \begin{matrix} \text{CH}_2\text{—NH}_2 & \quad & \text{NH}_2\text{—CH}_2 \\ | & \searrow \quad \swarrow & | \\ \text{CH}_2 & \text{Pt} & \text{CH}_2 \\ | & \diagup \diagdown & | \\ \text{NH}_3+ & \text{Cl} \quad \text{Cl} & \text{NH}_3+ \end{matrix} \end{bmatrix} \bar{\bar{P}}\text{tCl}_4 \xrightarrow{\text{NaOH}}$$

$$\begin{bmatrix} \begin{matrix} \text{CH}_2\text{—NH}_2 & & \text{NH}_2\text{—CH}_2 \\ | & \searrow \nearrow & | \\ & \text{Pt} & \\ | & \nearrow \searrow & | \\ \text{CH}_2\text{—NH}_2 & & \text{NH}_2 \quad \text{CH}_2 \end{matrix} \end{bmatrix} \text{PtCl}_4$$
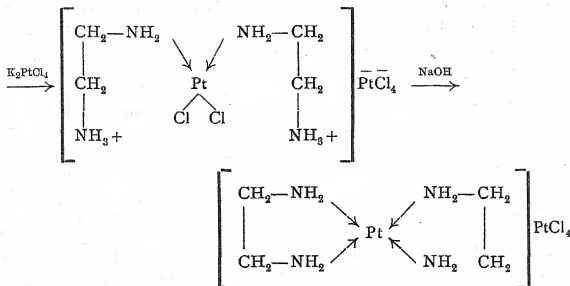
Nomenclature of the Co-ordination Compounds—When the group NH_3 occurs in a co-ordination compound it is called an ammine, ammoniate or ammino-compound. The other groups, whether negative radicals or neutral groups, are indicated by the addition of the ending -o to their ordinary names. Thus chloro-, sulphato-, carbonato- indicate co-ordinated Cl, SO_4 and CO_3. Aquo- indicates co-ordinated water, hydroxylo- or hydroxo- co-ordinated OH, oxo- co-ordinated O, and so on. The names of the groups in the complex precede that of the central metal, and their number is indicated by Greek ordinals, thus :

$$\begin{bmatrix} \text{Co}\begin{matrix}(\text{NO}_2)_3 \\ (\text{NH}_3)_3\end{matrix} \end{bmatrix}$$ trinitrito-triammine-cobalt. $$\begin{bmatrix} \text{Pt}\begin{matrix}\text{Cl}_2 \\ (\text{NH}_3)_2\end{matrix} \end{bmatrix}$$ dichloro-diammine platinum.
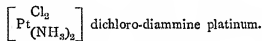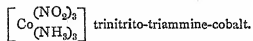
If the complex is a cation, it is named before the anion :

$$\begin{bmatrix} \text{Co}(\text{NH}_3)_6 \end{bmatrix}(\text{NO}_3)_3$$
hexammine-cobaltinitrate

$$\begin{bmatrix} \text{Co}\begin{matrix}(\text{NH}_3)_4 \\ (\text{H}_2\text{O})_2\end{matrix} \end{bmatrix}\text{Cl}_3$$
diaquo-tetrammine-cobaltichloride

$$\begin{bmatrix} \text{Co}\begin{matrix}(\text{NH}_3)_5 \\ \text{Cl}\end{matrix} \end{bmatrix}\text{Cl}_2$$
chloro-pentammine-cobaltichloride

$$\begin{bmatrix} \text{Co}\begin{matrix}(\text{NH}_3)_4 \\ \text{I}_2\end{matrix} \end{bmatrix}\text{Cl}$$
di-iodo-tetrammine-cobaltichloride

$$\begin{bmatrix} \text{Pt}\begin{matrix}(\text{NH}_3)_4 \\ (\text{OH})_2\end{matrix} \end{bmatrix}\text{Cl}_2$$
dihydroxo-tetrammine-platinic chloride

$$\begin{bmatrix} \text{Cr}\left(\text{OC}\begin{matrix}\diagup\text{NH} \\ \diagdown\text{NH}_2\end{matrix}\right)_6 \end{bmatrix}\text{Br}_3$$
hexa-urea-chromibromide.

The term ammine is placed immediately before the name of the metal and after the other constituents have been stated.

If, on the other hand, the complex is an anion, the compound is named as in the following examples :

$$\text{K}_3\begin{bmatrix} \text{SbCl}_6 \end{bmatrix}$$
potassium hexachloroantimonite

$$\text{K}_2\begin{bmatrix} \text{U}\begin{matrix}\text{O}_2 \\ \text{Br}_4\end{matrix} \end{bmatrix}$$
potassium di-oxo-tetrabromouranate.
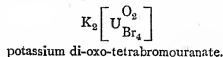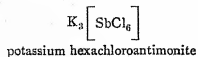
Werner's proposals for nomenclature were slightly different from these, and, while perhaps more logical, the results are more cacaphonous.[1]

Isomerism in Co-ordinated Compounds.—There are several pos-

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[1] See his *Neuere Auschauungen*, 4th edn., p. 94.

sibilities of isomerism in co-ordination compounds as can be seen from a consideration of the following types.

(a) *Polymerisation.*—This is well exemplified by

$$[Pt(NH_3)_2Cl_2] \quad , \quad [Pt(NH_3)_4][PtCl_4] \quad , \quad [Pt(NH_3)_3Cl]_2[PtCl_4].$$
$$\text{I.} \qquad\qquad\qquad \text{II.} \qquad\qquad\qquad \text{III.}$$
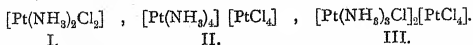
for II is the dimeride of I, and III is a trimeride. II is the green salt of Magnus (p. 337), and can be prepared by the double decomposition

$$[Pt(NH_3)_4]Cl_2 \;+\; H_2[PtCl_4] \longrightarrow 2\,HCl + [Pt(NH_3)_4]\,[PtCl_4]$$

The compounds $(CH_3)_2TeI_2$ and $[Te(CH_3)_3]^+[Te(CH_3)I_4]^-$ (p. 349) are exactly analogous. In the group of 6-co-ordinated compounds, Werner described nine polymeric forms of $[Co(NH_3)_3(NO_2)_3]$; the following show some of the formulations

$$\left[Co\dfrac{(NH_3)_3}{(NO_2)_3}\right] , \quad \left[Co\dfrac{(NH_3)_4}{(NO_2)_2}\right]\left[Co\dfrac{(NH_3)_2}{(NO_2)_4}\right] , \quad \left[Co\dfrac{(NH_3)_5}{(NO_2)}\right]\left[Co\dfrac{(NH_3)_2}{(NO_2)_4}\right]_2,$$

$$\left[Co(NH_3)_6\right]\left[Co\dfrac{(NH_3)_2}{(NO_2)_4}\right]_3 , \quad \left[Co\dfrac{(NH_3)_5}{(NO_2)}\right]_3\left[Co(NO_2)_6\right]_2.$$
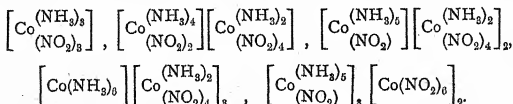
The existence of the metaphosphates $(NaPO_3)_x$, where $x = 1$ to 6 (see p. 727) is to be explained, at least in part, in this way.

(b) A simple cause of isomerism arises from the same radical occupying first an ionisable position outside the complex, and secondly a non-ionisable position inside the complex, *e.g.*:

$$\left[Co\dfrac{Br}{(NH_3)_5}\right]SO_4 \qquad\text{and}\qquad \left[Co\dfrac{SO_4}{(NH_3)_5}\right]Br$$
bromo-pentammino-cobaltisulphate.   sulphato-pentammine-cobaltibromide.
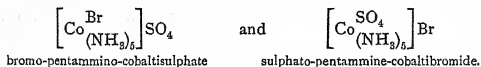
Both have the same empirical formula, but the second gives a precipitate of AgBr with silver nitrate, but no precipitate with $BaCl_2$, whereas the first is precipitated by $BaCl_2$ and not by $AgNO_3$. In like manner $[Pt(NH_3)_4(OH)_2]SO_4$ behaves as a neutral sulphate, and $[Pt(NH_3)_4(SO_4)](OH)_2$ has the properties of a strong base.

(c) Compounds are known, such as

$$[Co(NH_3)_6]\,[Cr(CN)_6] \qquad\text{and}\qquad [Cr(NH_3)_6]\,[Co(CN)_6]$$
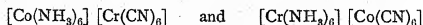
which are isomeric and not identical, for in the first cobalt is in the cation, chromium in the anion, whereas in the second the situation is reversed.

(d) The green and violet forms of $CrCl_3$, $6H_2O$ (see p. 278) can exist in solution in equilibrium which is only reached slowly, and depends on temperature, concentration and the nature of the other ions present. The green form is obtained on reducing chromates with

hydrochloric acid, evaporating the solution and finally precipitating the chloride by passing in HCl gas. The violet form can be produced by heating the 50 per cent. solution of the green salt to 80° for a few minutes, followed by cooling and saturation with HCl. It is also formed when a cooled solution of violet chrome alum is saturated with hydrochloric acid.

The green salt is granular or forms scales; the violet is a somewhat grey powder in the solid state. Both are deliquescent and very soluble in water, the violet somewhat more so than the green. Accurate measurement of the solubility is impossible, as reversion occurs rapidly in concentrated solutions. Further, the green salt can take up four more molecules of water at low temperatures; it is also soluble in alcohol but not in ether.

According to the work of Werner and Gubser,[1] two of the chlorine atoms in the green salt are more closely attached to the metal atom than the third, whereas in the violet salt all three chlorine atoms dissociate easily. In the green, moreover, four of the water molecules, and in the violet all six, are closely attached to the metal atom. These facts are expressed in the following formulae:

$$\left[Cr \begin{matrix} Cl_2 \\ (H_2O)_4 \end{matrix} \right] \begin{matrix} Cl \\ (H_2O)_2 \end{matrix}, \qquad\qquad \left[Cr(H_2O)_6 \right] Cl_3.$$

<center>Green.   Violet.</center>

The following considerations are advanced in support of these formulae:

1. When silver nitrate is added to the violet salt the whole of the chlorine is precipitated, showing that it is all in the ionic condition. Only a third of the total chlorine is precipitated as AgCl from the green salt, indicating that the other two-thirds is not present as anions.[2]

2. Determinations of conductivity and molecular weight show that the violet salt forms more ions per molecule than the green. For instance, the conductivities of $N/125$ solutions at 0° are:

Time				0	24	88 hours.
Green salt	.	.	.	52·6	115·9	164·2
Violet salt	.	.	.	174·7	...	...

The unequal conductivity of the green salt is lower, as at low temperatures the violet form is the more stable, and the green is slowly transformed into it. The number of ions produced can also be found by cryoscopic measurements. The freezing point of water is lowered twice as much on addition of the green chloride as it would

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[1] *Ber.*, 1901, 34, 1579.

[2] This effect is observed only in the presence of a little nitric, sulphuric or per-chloric acid. In neutral solution or in presence of weak acids more than one atom of chlorine is precipitated. The silver chloride must also be filtered off at once or more will again be formed, as equilibrium is slowly attained by the conversion of the green salt into the more ionised violet one. If excess of silver nitrate is used more chlorine will also be precipitated than is warranted by the above formula.

be if the salt were not dissociated at all, *i.e.* it is a binary electrolyte. The violet salt, however, gives four times the normal depression showing dissociation into four ions.

3. When dried over sulphuric acid the crystals of the violet chloride lose none of their water, while those of the green salt lose two molecules, showing that these are more loosely attached. The green salt remains green after this loss of water, showing that no fundamental change has occurred in its structure, but on prolonged desiccation it turns violet owing to the breaking up of the nucleus $[Cr(Cl)_6(H_2O)_4]'$, to which the green colour is due. On wetting with water it becomes green again, showing that the new nucleus is not identical with that of the violet chloride, which gives a violet solution; the inner chlorine atoms have not become detached from the chromium atom during drying.

The equilibrium between the two forms at moderate temperatures was studied by Olie,[1] who noticed that high temperature and high concentration favour the existence of the green salt, the violet solution becoming visibly greener on warming. In the experimental results given in the table below it can also be seen that at low temperatures and in dilute solution the violet form alone exists, while in higher concentration the two forms are present in about equal proportions.

Total Percentage of Chromium Chloride in the Solution at 25°.	Content per cent. of	
	Violet Salt.	Green Salt.
9·22	100·00	0
32·4	89·91	10·09
49·6	74·23	25·77
60·05	58·57	41·43

The presence of H˙ ions retards the conversion of the violet into the green form, and the green solution becomes violet at once when H˙ ions are removed.

A compound intermediate between the two forms appears to be formed as a pale green substance giving a bluish green solution in water.[2] The reactions of this salt indicate that one of the Cl atoms is co-ordinated with the Cr atom, and Bjerrum gives it the following formula:

$$\left[Cr_{(H_2O)_5}^{Cl}\right]Cl_2(H_2O).$$
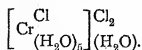
The other halides of tervalent chromium exist in isomeric forms like those of the chloride. The fluoride and thiocyanate show the usual violet-green isomerism, while the bromide gives a hydrate which is partly blue and partly green.[3] Isomeric double halides are formed not only with chromium as the central metal, but also with vanadium

[1] *Z. anorg. Chem.*, 1906, 51, 41.
[2] Bjerrum, *Ber.*, 1906, 39, 1599; *Z. physikal. Chem.*, 1907, 59, 596; Weinland and Schumann, *Ber.*, 1907, 40, 3093.
[3] Werner and Gubser, *Ann.*, 1902, 322, 343.

(green and raspberry red) and titanium (green and violet). The violet form of the titanium salts is the more stable. In the green double halides of chromium the large ion of the green chromium chloride is unchanged, two atoms of chlorine are not precipitated by silver nitrate, and four of the water molecules are more closely attached than the rest. The violet double salts are known only in the solid state, as in presence of acid they are rapidly converted into the green form, a process only somewhat restrained by an excess of alkali halide in solution. On the other hand, the green salts pass into the violet form on crystallisation. The violet forms usually have less than six molecules of water of crystallisation, and so are not exactly analogous to the simple violet chromium chloride.

Water may be bound in such complexes by field valency forces (see p. 302), and possibly also polymerised water molecules, $e.g.$ $(H_2O)_2$ or $(H_2O)_3$, may occupy a single co-ordination position.

(e) Isomerism can also be due to space arrangement in the complex. There are, for example, two series of compounds, both of which contain the univalent cation $\left[Co \begin{array}{c}(NH_3)_4\\(NO_2)_2\end{array} \right]^{\cdot}$, and which do not differ much in their reactions, but can be distinguished by the physical properties of their derivatives. According to Werner, this isomerism is due to the different arrangements of the groups in the octahedron. There are obviously two different ways of arranging the groups: either they are adjacent to each other (the cis or 1 : 2 position) or they are at opposite corners of the octahedron (the trans or 1 : 6 position); there are no other possible arrangements in this compound (see Fig. 44).
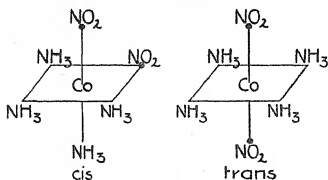
FIG. 44.
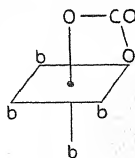
FIG. 45.

Many compounds of the type $\left[M \begin{array}{c}a_2\\b_4\end{array} \right]$ show isomerism of this kind, and in no case have more than two isomers been isolated, a limit required by the octahedral space formula. It is possible to find which of the isomers corresponds to the cis and which to the trans position. In one set of isomers both NO_2 groups are replaced by

dibasic acid radicals such as CO_3'', while in the other form no substitution can be made to take place. The form in which substitution occurs is probably the cis form, as shown in Fig. 45. For if it took place in the trans position the CO_3 group would have a much longer span than is likely from its behaviour in organic compounds; inversion of configuration may, however, take place during the substitution (see pp. 298-9). If the space arrangement is octahedral, the compound $\left[M \begin{smallmatrix} a_3 \\ b_3 \end{smallmatrix} \right]$ should also have two isomers, the compounds
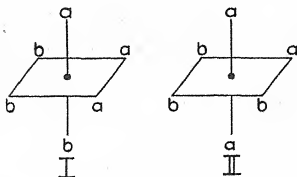
There is one cis position (I) and one trans position (II), without the possibility of a third arrangement. When one of the a groups is replaced by a b group, only a cis compound is formed from (I), while

cis trans
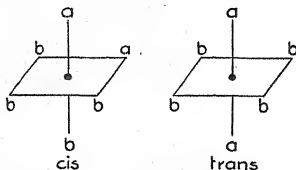
both cis and trans forms can arise from (II); this is in agreement with the experimental results. In this way the isomers can be identified, the cis form giving a single product while the trans compound gives some cis derivative on substitution. It was found that the substances thought to be cis compounds were the same whether determined by the action of dibasic acids or by substitution in the tri-derivatives.

The theory of an octahedral arrangement is confirmed still further by the existence of optically active isomers. A compound rotates the plane of polarised light when a mirror image of the molecular model exists which cannot be superimposed on the original model. Isomerism of this type occurs in octahedral structures of the type $[M(R_2)_3]$, in which R_2 represents a chelate group, e.g. the oxalate

radical or ethylenediamine. The following diagrams show the mirror image forms of compounds of this type:
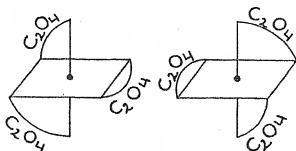
These two figures cannot be superimposed. Compounds of this kind, when synthesised, appear as inactive mixtures of the two isomers (racemic mixtures), and the isomers, if bases, must be separated by recrystallisation as salts of optically active acids, *e.g.* of brom-camphor-sulphonic acid. When the compounds are acids they must be recrystallised as salts of optically active bases, *e.g.* strychnine. Werner accomplished the separation in numerous instances (1912-18). Rhodium, iridium, platinum, cobalt, chromium, etc., were used as central atoms, and ethylenediamine, propylenediamine, oxalic acid and even OH groups, as in the compound

$$\left[Co \left\langle \begin{array}{c} H \\ O \\ O \\ H \end{array} Co(NH_3)_4 \right\rangle_3 \right] X_6 .$$
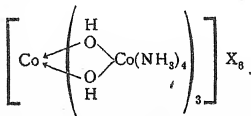
were used as co-ordinated groups in the optically active compounds; in the one figured the OH groups occupy the two adjacent corners of the octahedron.[1] The optically active substances thus formed do not contain carbon as the central atom—some of them contain none at all, for example the Co compound above and the Rh compound below—so that the activity cannot be due to that element. The specific rotation of these compounds is often extremely high, and may amount to several thousand degrees—much greater than that of organic compounds.

Further evidence concerning *cis-* and *trans-*configurations is obtained from possible asymmetry of the *cis-*forms, which is absent in the *trans-*

variety, *e.g.* for [Co en₂Cl₂]Cl the *cis-*form is asymmetric,
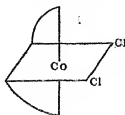
[1] *Ber.* 1914, 47, 3087.

and therefore resolvable, whereas the *trans*-form is symmetrical, and accordingly can be obtained only in an inactive form. Violeo-[Co en$_2$Cl$_2$]Cl has been resolved, and is therefore *cis*- and by analogy [Co(NH$_3$)$_4$Cl$_2$]Cl is the *cis*-form, whereas praseo- [Co en$_2$Cl$_2$]Cl is irresolvable, and is thus the *trans*-isomer. The arguments and facts are the same for compounds such as

$$\left[\begin{array}{c} \text{Co} \\ \text{Cl} \end{array} \right]^{\text{NH}_3} \text{Cl}_2 \quad \text{and} \quad \text{Na} \left[\begin{array}{c} (\text{H}_2\text{O}) \\ (\text{H}_2\text{O}) \end{array} \right> \text{Rh} \left< \begin{array}{c} \text{NH} \\ \text{NH} \end{array} \right> \text{SO}_2 \right)_2 \right]$$
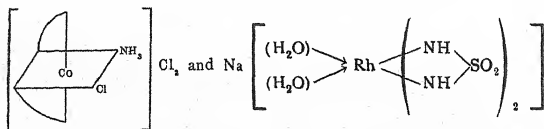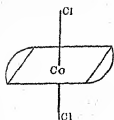
The last, a purely inorganic compound, *cis*-sodium diaquo-disulphamido-rhodium was resolved by Mann[1] into *d*- and *l*-forms.

Inversion Phenomena.—Inversion of configuration may take place during reactions of co-ordination compounds of metals; just as in carbon compounds, these inversions may be both of the geometrical and the Walden Inversion types.

(a) *Geometrical Inversion.*— Such inversions are mentioned on p. 316, *e.g.*:

$$trans - [\text{Co en}_2\text{Cl}_2]\text{Cl} \quad \xrightarrow[\text{HCl}]{\text{Evaporate in neutral solution}} \quad cis - [\text{Co en}_2\text{Cl}_2]\text{Cl}$$

$$cis - [\text{Co(NH}_3)_4\text{CO}_3]\text{X} \quad \xrightarrow{\text{MHSO}_3} \quad cis - \text{ and } trans - \text{M[Co(NH}_3)_4(\text{SO}_3)_2].$$
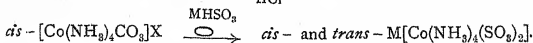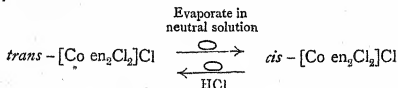
As other examples, there are:

$$cis - [\text{Co(NH}_3)_4(\text{CO}_3)]\text{NO}_3 \searrow$$
$$\xrightarrow{\text{HCl+Heat}} trans - [\text{Co(NH}_3)_4\text{Cl}_2]\text{Cl}$$
$$cis - [\text{Co(NH}_3)_4(\text{C}_2\text{O}_4)]\text{Cl} \quad \nearrow_{\text{HCl, H}_2\text{SO}_4+\text{Heat}}$$
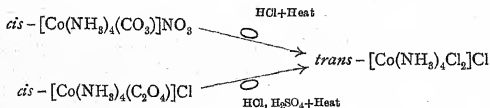
Mann, Crowfoot, Gattiker and Wooster[2] studied the following transformations of 4-co-ordinated palladium compounds, and determined the structures by X-ray analyses:

$$trans - [\text{Pd(NH}_3)_2\text{Cl}_2] \xrightarrow{\text{K}_2\text{C}_2\text{O}_4} cis - [\text{Pd(NH}_3)_2(\text{C}_2\text{O}_4)]$$
$$\searrow_{\text{NaNO}_2}$$
$$\xrightarrow{} trans - [\text{Pd(NH}_3)_2(\text{NO}_2)_2]$$
$$cis - [\text{Pd(NH}_3)_2(\text{NO}_2)_2] \quad \nearrow_{\text{Hot Water}}$$
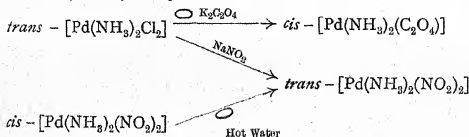
[1] *Nature*, 1932, 130, 368 ; *J. Chem. Soc.*, 1933, 412.   [2] *J. Chem. Soc.*, 1935, 1642.

The *trans*-modifications of such palladium complexes are usually more stable than the *cis*-forms.

(b) *Walden Inversion.*—Although many reactions of this type have been observed in carbon chemistry, very little has been done on this aspect of substitution in connection with metallic complexes. Bailar and Auten[1] made the following observations, which involve a change in configuration during substitution :

$$l-[\text{Co (en)}_2\text{Cl}_2]\text{Cl} \underset{\text{HCl}}{\overset{\text{K}_2\text{CO}_3}{\rightleftharpoons}} d-[\text{Co (en)}_2(\text{CO}_3)]_2\text{CO}_3$$

$$\downarrow \text{Ag}_2\text{CO}_3$$

$$l-[\text{Co (en)}_2(\text{CO}_3)]_2\text{CO}_3$$
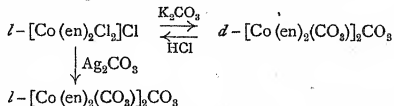
Both potassium and silver oxalates, however, yield the *d*-oxalato-compound from the *l*-chloro-compound.

Chief and Auxiliary Valencies.—A good deal of controversy has arisen from time to time as to the mode of combination in co-ordinated compounds. The ability to combine with molecules which can exist separately was often called a secondary (or auxiliary) valency, and was supposed to be different in nature from the force which holds together the Na and Cl atoms in common salt. But in the space formulae of the co-ordinated compounds no difference can be detected between the primary valencies and the secondary ones; radicles or whole molecules enter the octahedron on the same footing. The occupants of the corners of the octahedron can be joined to the central atom either by primary or by secondary valencies. It may be noted, moreover, that complexes exist in the crystals of the most simple substances. Fig. 46 shows the crystal lattice of the halide of an alkali metal. The black atoms represent those of the alkali metal, the light ones those of the halogen. If the metal atom in the centre of the cube is considered it can be seen that it is in the centre of six halogen atoms, which occupy the corners of an octahedron surrounding it. If one imagines the lattice to be enlarged to include the halogen atom lying in the next molecule, it can be seen that this atom is also at the centre of an octahedron with metal atoms at its corners. Thus the crystal is not built up of single NaCl molecules, but is a single giant molecule built up of Na(Cl)_6 and Cl(Na)_6 groups interlaced; so that polar compounds may be considered as complex compounds when in the form of crystals.[2]
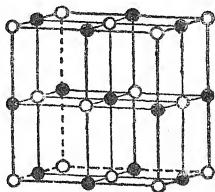
FIG. 46.—Crystal lattice of the alkali halides (except caesium chloride).

There is, however, an obvious distinction between the neutral groups

[1] *J. Amer. Chem. Soc.*, 1934, 56, 774.
[2] Pfeiffer, *Z. anorg. Chem.*, 1916, 97, 161.

in a complex, which never appear in the ionic condition, and the units which do not exist separately except as ions. That is, a distinction arises when the groups become separate from the complex. In the early development of the theory of valency the charge which the atom or group could take up was kept in view; and valency in the electro-chemical sense was an exclusive property of the radicals which were incapable of separate existence. Thus the ionic primary valency was emphasised and the addition of neutral groups regarded as a casual activity of the atom, rather than a necessary feature of the production of stable structures. It is clear that there is a great deal to be said against this view. The combination of AuCl and Cl_2 to form $AuCl_3$, or that of Ca and H_2 to form CaH_2, is between substances which are quite stable by themselves. Yet these reactions are regarded as resulting in an alteration in the primary valency because compounds are known in which gold is electro-chemically tervalent and calcium bivalent. If, however, the views on the formation of compounds developed on p. 11 are adopted, the difference between primary and secondary valencies almost entirely disappears. For even in the addition of saturated groups an alteration in the electric field—that is, in distribution of the electrons—takes place.

The binding forces of co-ordinated groups are very variable and the stability of the resulting compounds varies accordingly. There are, on the one hand, complexes of low stability, such as the double halides of metals (e.g. $KMgCl_3 . 6H_2O$), and, on the other hand, some which cannot be dissociated unless fundamental decomposition of the compound takes place, e.g. Na_3AlF_6 or $K_3[Fe(CN)_6]$ or $K_3[Co(CN)_6]$ and complexes of every degree of stability intermediate between these extremes are known. Steric effects have no little influence on the stability of the complex, and much remains to be found out about their effect. Even the portions of the compound which lie outside the complex have a very definite influence on the effectiveness of the co-ordination; thus the cationic complex $[M(NH_3)_6]^{..}$ is most stable when in combination with I' or ClO_4' ions, less so with CH_3COO' ions, while no compound of it with CO_3'' is known. These effects will be considered later.

The co-ordination valencies are in no sense subordinate to or weaker than the primary valencies. The energy developed when they operate, usually evident as evolution of heat, is often much greater than that caused by some primary valencies. Thus Ag_2O is much more easily decomposed than the complex $[Ag(NH_3)]'$; $[Cu(H_2O)]^{..}$ is similarly more stable than CuI_2, and many other instances might be quoted. Further, the co-ordination valencies must not be regarded as residual valencies which are left over when the primary valencies have been used up; actually they are more potent rather than less when the other valencies are all occupied. This is well shown by the tenacity with

which neutral groups are held by compounds of the same metal in different stages of oxidation.

Thus, for example, NH_3 is more closely attached to $Cu^{..}$ than to $Cu^{.}$ compounds, to $Cr^{...}$ than to $Cr^{..}$, to $Co^{...}$ than to $Co^{..}$, to $Pt^{....}$ than to $Pt^{..}$, and so on. Only in iron salts is the ammonia more firmly attached to the -ous form.

Accordingly, compounds due to primary valencies often become more stable when co-ordination comes into play. Thus the unstable CuI_2 is less easily decomposed when NH_3 is present in the molecule, and a stable compound of formula $[Cu(NH_3)_6]I_2$ is known. Compounds of bivalent silver (p. 699) and of univalent copper (p. 700) are also rendered stable. Similarly, whole groups of salts like the nitrites of the heavy metals are unknown except as complexes, and it is likewise impossible to dehydrate some hydrated salts (e.g. the sulphites of the heavy metals) without decomposition of the anhydrous form. When the complex hydrate is broken up the salt molecule is rearranged, in these salts, into sulphide and sulphate. No cyanides of tervalent metals are known except complex cyanides, and the hydroxide is the only simple tervalent compound of cobalt which has been prepared, while complex compounds of tervalent cobalt are plentiful. The same is true of the compounds of quadrivalent manganese. The operation of co-ordination thus allows compounds to be made whose existence would not otherwise be suspected, and the primary valency is itself often enhanced in value when they come into action. The co-ordination valencies must not therefore be regarded as primary valencies split up into parts. The views of Linus Pauling on bonds in complex compounds have already been discussed (p. 56). The concept of hybrid bond orbitals satisfactorily explains the marked stability of these bonds, as well as their orientation, while their nature may be visualised by applying the ideas of resonance referred to in Chapter II.

Co-ordination not only stimulates the primary valencies, but may also bring into play secondary valencies from other parts of the molecule, and further neutral groups can thus be added. This seems to occur most readily when the added portions have a large volume, and salts which contain large molecules like caffeine or hexamethylenetetramine can take up unusually large quantities of water of crystallisation. The alkali polyiodides combine with aniline, etc., whereas the ordinary alkali iodides do not. It is not known at what point in the molecule these new groups enter. When the central atom lies between two very voluminous radicals the co-ordination number increases in value; thus that of Ni, which is normally 6, rises to 8 in the octammine of nickel benzoate, $(C_6H_5COO)_2Ni \cdot 8NH_3$ and in

$$\left[Co\frac{(NO_2)_4}{(NH_3)_2}\right]_2 Ni(NH_3)_8.$$
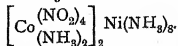
The additional ammonia molecules may be held by field valency forces

Possibly the space arrangement about the central atom is particularly favourable—it appears to lie in a hollow which can be filled up with neutral groups.[1]

The Field Valency Theory.—There is a large number of compounds which were previously described as due to secondary valencies and which cannot be assigned to the co-ordination class. These are now known as field valency compounds.

If matter is regarded as built up of positively and negatively charged particles placed at a certain short distance from one another, there must be electric fields of force between these particles. In polar molecules these fields must also exist—in the NaCl molecule the sodium atom forms a positive and the chlorine atom a negative pole, and between the two is a field of force. A second molecule of NaCl approaching the first will try to dispose itself so that its positive part is near the negative part of the first molecule and *vice versa.* As the electric forces act in all directions in space further new molecules will arrange themselves in three dimensions to form a symmetrical giant molecule, which can at once be recognised as a crystal. These structures are thus formed under the action of field valencies, and show all the transitions between electrovalency and covalency.

The field valency is responsible for addition reactions in which the sharing of electrons plays no obvious part, as in the formation of readily decomposed compounds such as hydrates, ammines and double salts. A few examples will now be mentioned to illustrate this aspect of valency.[2]

In such field valency compounds, the neutral molecules (water, etc.), which often cannot be accounted for satisfactorily by co-ordination theory, may, in a sense, be supposed to fill the seams or vacant spaces of the crystal lattice, and thus to stabilise the whole structure. The building may be regarded as geometrical, the cavity in the lattice being suitably filled by the entering group, but the relatively small electric forces associated with the units must support and not oppose the building. Sidgwick[3] uses the term "van der Waals' force" (which is related to *a* of van der Waals' equation) for this field valency effect. These views agree with the determinations of crystal structure as revealed by X-ray analysis: Cox,[4] for example, showed that in $[Pt(NH_3)_4]Cl_2, H_2O$, the water, which is over and above the number of groups required by co-ordination theory, forms the centre of the crystal unit, the other groups being assembled about it. This corresponds with the difficulty experienced in removing water of crystallisation from this

[1] Ephraim, *Ber.*, 1918, 51, 644; 1920, 53, 548.
[2] For a more exhaustive discussion see Ephraim, *Chemische Valenz- und Bildungslehre*, Leipzig, 1928, p. 259.
[3] *The Covalent Link in Chemistry*, Oxford, 1933, Chap. I. *J. Chem. Soc.*, 1941, 433.
[4] *J. Chem. Soc.*, 1932, 1912.

compound; the water cannot be regarded as linked by anything more than field valency, but owing to its geometrical disposition, it is held very stably. The solid hydrates of the inert gases (see p. 61) and of the paraffins are no doubt of a similar type. These views are closely allied to those put forward by Hägg (see pp. 852 and 853) in connection with carbides, silicides, borides, etc. The co-ordination number of seven, observed particularly in complex fluorides (see p. 357), may arise from field valency effects; thus $(NH_4)_3HfF_7$ has been shown crystallographically to consist of units of $(NH_4)_3HfF_6$ and NH_4F. Furthermore, the presence of the large numbers of molecules of water of crystallisation and of ammonia, associated particularly with certain halides (see p. 332) may be considered to be due to field valency effects but adsorption may also play a part.

Double Halides of the Tervalent Metals.—Returning to the starting-point of this discussion (p. 279), the structure of the double halides of the tervalent metals, it is found that the stability of the double salts is not the same for all the halogens, the order being: cyanides, fluorides, thiocyanates, chlorides, bromides, iodides. The last three give strong complexes only with gold, and their full power is only developed in combination with quadrivalent metals.

Besides the complex fluorides of tervalent vanadium mentioned on p. 279, those of tervalent manganese are known, e.g.

$$\left[Mn^{F_5}_{(H_2O)} \right] M_2^I.$$
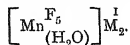
These compounds are dark red, almost black in the solid state, and give dark red solutions. The chromium double fluorides of the type

$$\left[Cr^{F_5}_{(H_2O)} \right] M_2^I \text{ and } \left[CrF_6 \right] M_3^I$$
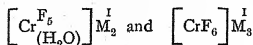
are insoluble in water; those of aluminium and iron are also insoluble, and occur as important minerals in nature of the types

$$3MF, AlF_3, \quad 2MF, AlF_3, \quad MF, AlF_3,$$
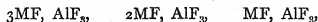
with a water content to make up the number of co-ordinated groups to six.

The double chlorides, bromides and iodides display isomerism, as discussed on p. 293, which is easily explained by the co-ordination theory. They are often not strongly complex, but $BiCl_3$, for example, is soluble in water without hydrolysis if sufficient alkali chloride is present. Compounds of the type $2M^{III}Cl_3 . 3M^ICl$ show that in the double salts polymerisation of MCl_3 to a double molecule occurs, e.g. in these compounds of Al, Bi and W. Gold gives the most stable complexes of any tervalent metal and the free complex acid $[AuCl_4]H$ can be crystallised with 4 mols. of water. It is prepared by dissolving

gold in excess of *aqua regia*, and forms pale yellow needles. Hittorf showed as long ago as 1859[1] that the salts of this acid were complex in solution and that gold went to the anode on electrolysis. The heavy metal salts of this acid crystallise with many mols. of water of crystallisation (8-12), an example of the increase in the power of adding neutral groups when a small cation is combined with two voluminous anions (p. 301). The water content increases with diminishing atomic volume of the metal. The number of mols. of water decreases from 12 for the smallest metals to 6 for those of mean volume, to 2-4 for the smaller alkali metals, and is zero in the salts of the larger alkali metals and of organic bases. When the cation is very large the salt is insoluble, and hence this acid can be used as a precipitant for complex cations, like those of tervalent cobalt or of the alkaloids. The complex iodides of gold containing the ion $[AuI_4]'$ are stable—much more so than the simple iodide AuI_3—and form black crystals.

$RuCl_3$ (red) in aqueous alcohol gives with HCl the compound $H[RuCl_4 2H_2O]$ in red (*cis*-) and green (*trans*-) forms. $K_2[RuCl_5 H_2O]$ is also stable and is dehydrated with difficulty.

Double thiocyanates of the type

$$\left[\overset{\text{III}}{M}(CNS)_6\right]M_3^{\text{I}}, aq.$$
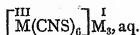
are the most common, only that of gold having the formula $[Au(CNS)_4]M^I$. They vary a good deal in the stability of the complex, the brilliantly red double thiocyanate of vanadium, $[V(CNS)_6]M^I_3$, $4H_2O$, the violet salt of titanium, $[Ti(CNS)_6]M_3$, $6H_2O$, and that of chromium being among the most stable. Neither Cr nor CNS ions can be detected in the wine red $[Cr(CNS)_6]H_3$, which is stable in acid solution. The stable salts $M_3[Rh(CNS)_6]$ also give the free acid $H_3[Rh(CNS)_6]$.

The double ferric thiocyanates are of practical importance as a test for ferric or thiocyanate ions owing to the use of the red colour of the undissociated $Fe(CNS)_3$. With excess of KCNS a double salt is formed, of composition $K_3[Fe(CNS)_6]$ which is isomorphous with the corresponding scandium complex; it is violet in colour, but is decomposed by water, with formation of the deep red $Fe(CNS)_3$. It is possible to dissolve it unchanged in alcohol to a violet solution.[2] When the simple salt $Fe(CNS)_3$ is diluted in a solution which is not acid, it is hydrolysed to $Fe(OH)_3$ and HCNS, thus losing its red colour. If acid is present the hydrolysis is repressed, and thus the red colour persists. In absence of acid the red colour is not produced even in excess of KCNS, as no Fe··· ions are available when the solution is sufficiently dilute for hydrolysis to occur. In fairly concentrated solutions an excess of either KCNS or Fe··· ions deepens the red

[1] *Pogg. Ann.*, 106, 523.
[2] Rosenheim and Cohn, *Z. anorg. Chem.*, 1901, 27, 296.

colour, for either of them decrease the ionisation of the $Fe(CNS)_3$ in accordance with the law of mass action, as the ionisation, though not very great, has an appreciable effect in reducing the coloration.

Complex Cyanides.—Double cyanides are among the most stable complexes known. They are mostly unaltered in acid solution, and differ in colour in a remarkable manner from the simple compounds of the metals they contain. The usual formula of the complex is $[M^{III}(CN)_6]'''$, but, as in the thiocyanates, the gold compounds are exceptional and contain the weaker complex $[Au(CN)_4]'$, which is decomposed. in acid solution. The liberated HCN does not give enough CN′ ions to move the equilibrium $Au(CN)_4' \rightleftharpoons Au(CN)_3 + CN'$ to the left and thus prevent precipitation of the simple cyanide. The salts of this complex are colourless and easily soluble in water, and the cyanogen groups can be replaced in part by other halogens, *e.g.* in

$$\left[Au \begin{matrix} (CN)_2 \\ I_2 \end{matrix} \right]'.$$
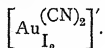
The complex $[M^{III}(CN)_6]'''$ is produced when solutions containing $M^{\cdots}$ ions are treated with CN′ ions; *e.g.* when excess of KCN is added to solutions of $M^{\cdots}$ salts or when the hydroxides are dissolved in KCN. Intermediate compounds are often formed on treating salt solutions with KCN; their composition is variable, and sometimes they dissolve only in boiling KCN. These complex cyanides can also be prepared by oxidation of $[M^{II}(CN)_6]''''$ compounds. Thus $K_3[Fe^{III}(CN)_6]$ can be made by oxidising $K_4[Fe^{II}(CN)_6]$ with chlorine, bromine, permanganate, or lead peroxide; but the reduction potential of the lower double cyanide is so small that oxidation of some compounds takes place even in the air; *e.g.* formation of $[Mn^{III}(CN)_6]'''$ from $[Mn^{II}(CN)_6]''''$ or of $[Co^{III}(CN)_6]'''$ from $[Co^{II}(CN)_6]''''$. Indeed, if air is absent, the latter radical $[Co^{II}(CN)_6]''''$ decomposes the water in which it is dissolved, and hydrogen is evolved, as in the action of vanadous and chromous compounds (p. 155).

The potassium salts of the double cyanides were among the first to be prepared. They are fairly soluble in water and crystallise easily. The sodium salts are much more soluble, as are also those of some of the heavy metals. The double cyanides of some of the heavy metals are insoluble precipitates of characteristic colour. The alkali salts of the chromium double cyanides are pale yellow, those of the double manganese cyanides dark red to black, of cobalt very pale yellow, and of ferric iron brownish red ("red prussiate of potash"). The alkali salts of the double cyanides of Cr, Mn, Co, Fe, Rh and Ir are isomorphous. The free complex acid is precipitated from solutions of the cobalt and iron compounds on addition of hydrochloric acid, *e.g.* $H_3[Fe(CN)_6]$, which forms brownish green needles. This acid is soluble in water and in alcohol, and forms addition products with ether and with

many other organic compounds containing oxygen; these products can be obtained by shaking the aqueous solution with the organic solvent. The organic constituent is lost when the solution is evaporated *in vacuo* and the pure acid is left; the acid $H_3[Co(CN)_6]$ is obtained in this way.[1] The addition compound was regarded by Baeyer as one of quadrivalent oxygen (*cf.* p. 221).

The precipitates formed when solutions of the alkali double cyanides are added to solutions of the heavy metals are mostly flocculent, slimy or gelatinous, and always contain alkali metals, but the nature of the substances makes it difficult to determine whether these are only adsorbed from solution or in chemical combination. There is no doubt, however, that the adsorption of alkali salts is an important factor. Among the best known compounds is that of ferricyanide, in which part of the potassium is replaced by ferrous iron (*Turnbull's Blue*, $Fe^{II}K[Fe^{III}(CN)_6]$). Its structure is substantially the same as that of the precipitate produced by ferric salts in solutions of ferrocyanide (*Prussian Blue*, $Fe^{III}K[Fe^{II}(CN)_6]$). It can be supposed that the ferricyanide ion has an oxidising, the ferrocyanide ion a reducing action, so that the former oxidises the $Fe^{..}$ outside the complex to $Fe^{...}$, while the latter reduces the $Fe^{...}$ to $Fe^{..}$. At the same time $[Fe^{III}(CN)_6]'''$ is reduced to $[Fe^{II}(CN)_6]''''$ and $[Fe^{II}(CN)_6]''''$ oxidised to $[Fe^{III}(CN)_6]'''$. Thus a mixture of the two salts is obtained, the composition of which depends on the relative quantities of the substances originally used. With excess of $Fe^{..}$ or $Fe^{...}$ ions the alkali content of the precipitate is reduced, so that it approximates to the composition $Fe^{II}_3[Fe^{III}(CN)_6]_2$ or $Fe^{III}_4[Fe^{II}(CN)_6]_3$, though it does not follow that its structure is that represented by these formulae. The properties of these compounds are very variable, owing to their colloidal nature. Sometimes the precipitates are obtained in the form of fine particles (*e.g.* when equimolecular quantities of $Fe^{..}$ salt and $K_3Fe(CN)_6$ react); sometimes they form voluminous insoluble precipitates, which may or may not go into solution on washing. If the reacting solutions are sufficiently concentrated and are mixed practically instantaneously, dark blue gels may be obtained. A very small amount of such a gel stirred into a large volume of pure water results in a sol which passes through filter paper. The precipitate or colloidal solution is also often green instead of blue, especially when formed from very dilute solutions. On ageing, all these products become dark blue and insoluble, but by suitable precautions in precipitating, permanent varieties can be prepared which differ in colour. The colloid is stable in the form in which it is dried. These compounds are extremely resistant to reagents; they are not soluble in acids even when freshly precipitated, and with alkalis colourless solutions are formed, from which the blue precipitate reappears on acidifying, if kept cold throughout.

[1] Baeyer and Villiger, *Ber.*, 1901, 34, 2579; 1902, 35, 1206.

FIG. 47.—Ferric ●. Ferrous ○. Alkali metal ⊕.

FIG. 48.—Ferrous ○. Alkali metal ⊕.

FIG. 49.—Ferric ●.

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FIG. 47.—Ferric ●.   Ferrous ○.   Alkali metal ⊕.

FIG. 48.—Ferrous ○.   Alkali metal ⊕.

FIG. 49 —Ferric ●.

Ferric salts give only a brown coloration with ferricyanides when the compound $Fe^{III}[Fe^{III}(CN)_6]$ might be expected to be formed. This material, *Berlin Green*, is obtained by the oxidation of Prussian blue in air. Ferrous salts give a white precipitate with ferrocyanide, of which the composition is $Fe^{II}K_2[Fe^{II}(CN)_6]$ or $Fe^{II}_2[Fe(CN)_6]$. It is oxidised to the blue compound in the air.

X-ray analysis applied to the structure of these compounds has given some interesting results.[1] The three types represent a progressive oxidation of ferrous to ferric. The structures are all cubic $(a = 10\cdot2$ Å) and commercial pigments tend to the intermediate formula, $Fe^{III}M[Fe^{II}(CN)_6]$. The $Fe^{\cdots}$ and $Fe^{\cdot\cdot}$ atoms are arranged alternately at the corners of cubes of side $5\cdot1$ Å, with the alkali metal atoms (or ammonium) at the centres of the alternate small cubes (Fig. 47). The white compound, $Fe^{II}M_2[Fe^{II}(CN)_6]$ has the atoms of iron similarly arranged but with alkali metal atoms in the centre of each small cube (Fig. 48). In Berlin green, $Fe^{III}[Fe^{III}(CN)_6]$, the iron atoms occupy the corners of the small cubes but with no alkali metal atoms within the cubes (Fig. 49). In each compound the (CN) groups lie in the edges of the small cubes.

Cupriferricyanides, $Cu^{II}M[Fe^{III}(CN)_6]$, exist and have the same structure as prussian blues with the edge of the cube slightly less than $10\cdot2$ Å.

The chemical properties of the ferricyanides are determined by their complexity and their oxidising action. The reactions of ferric iron with NaOH, $(NH_4)_2S$ or KCNS cannot be obtained with these compounds; in fact, iron as such can only be detected after ignition. Potassium ferricyanide is used as an oxidising agent, mostly in organic chemistry. It oxidises H_2S to sulphur, and in alkaline solution hydrogen peroxide is reduced by it with evolution of free oxygen. The yellow ferrocyanide is the usual product of reduction of ferricyanide.

The CN groups in the hexacyanide iron compounds can be replaced by other radicals, thus yielding some interesting compounds; those derived from the bivalent iron compounds can be oxidised by bromine to corresponding substances containing the metal in its tervalent form, and the latter are often made in this way. The most important derivatives are:

1. $\left[Fe\substack{(CN)_5 \\ NO}\right]Na_2, 2H_2O$ 2. $\left[Fe\substack{(CN)_5 \\ NH_3}\right]Na_3, 6H_2O$ 2a. $\left[Fe\substack{(CN)_5 \\ NH_3}\right]Na_2, H_2O$

$= 2NaCN, Fe(CN)_3, NO$ $3NaCN, Fe(CN)_2, NH_3$ $2NaCN, Fe(CN)_3, NH_3$

3. $\left[Fe\substack{(CN)_5 \\ CO}\right]K_3$ 4. $\left[Fe\substack{(CN)_5 \\ H_2O}\right]Na_3, 7H_2O$ 4a. $\left[Fe\substack{(CN)_5 \\ H_2O}\right]Na_2$

$= 3KCN, Fe(CN)_2, CO$ $3NaCN, Fe(CN)_2, H_2O$ $2NaCN, Fe(CN)_3, H_2O$

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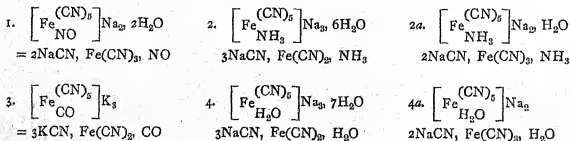
[1] Keggin and Miles, *Nature*, 1936, **137**, 577.

5. $\left[\text{Fe}\genfrac{}{}{0pt}{}{(\text{CN})_5}{\text{AsO}_3}\right]\text{Na}_4$, 10H$_2$O   6. $\left[\text{Fe}\genfrac{}{}{0pt}{}{(\text{CN})_5}{\text{NO}_2}\right]\text{Na}_4$, 10H$_2$O   7. $\left[\text{Fe}\genfrac{}{}{0pt}{}{(\text{CN})_5}{\text{NSO}}\right]\text{Na}_4$

= NaAsO$_2$, 3NaCN, Fe(CN)$_2$ NaNO$_2$, 3NaCN, Fe(CN)$_2$ NaNOS, 3NaCN, Fe(CN)$_2$

8. $\left[\text{Fe}\genfrac{}{}{0pt}{}{(\text{CN})_5}{\text{SO}_3}\right]\text{Na}_5$, 9H$_2$O

= Na$_2$SO$_3$, 3NaCN, Fe(CN)$_2$.
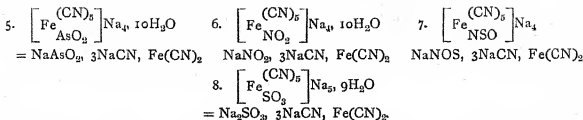
It can be seen from the double salt formulae printed under the complex formulae that these compounds, with the exception of Nos. 1, 2a and 4a, are all derived from bivalent iron. Recent work indicates that (1) also contains bivalent iron (see p. 681). Thus many of them can be oxidised (*e.g.* those with NH$_3$, H$_2$O and NO$_2$ as neutral groups), and K. A. Hofmann[1] found that oxidation normally occurs in two stages—prusso- and prussi-compounds being formed. He worked mostly with sodium nitroprusside (No. 1 in the above list), and obtained well-crystallised prusso-compounds which were yellow to reddish yellow in colour, and prussi-compounds which varied in colour from an intense carmine to bluish violet.

The radicals [Fe$^{\text{II}}$(CN)$_5$]''' and [Fe$^{\text{III}}$(CN)$_5$]'' have a lower valency than [Fe$^{\text{II}}$(CN)$_6$]'''' and [Fe$^{\text{III}}$(CN)$_6$]''', for the CN is not a neutral group but enters the complex as the CN' ion. When the CN is replaced by neutral groups such as NO, NH$_3$, CO, etc., as has occurred in the compounds, 1, 2, 3 and 4, the pentacyanide compounds produced have a lower valency than the hexacyanides from which they are derived. When, however, the CN' is replaced by a radical which is a univalent ion, the valency of the complex is unaltered, *e.g.* in Nos. 5 and 6, with the ions NO$_2$', AsO$_3$'. When the replacing ion has a valency higher than that of CN' the negative valency of the complex is increased, as in compound 8 above, where the CN is replaced by the bivalent SO$_3$''.

Sodium nitroprusside is the best known of the substituted cyanides and serves as a starting-point for the preparation of the others. It is obtained by the oxidation of potassium ferrocyanide with dilute nitric acid and subsequent neutralisation of the liquid with sodium carbonate. It is used in analysis as a test for soluble sulphides, with which it gives an intense violet colour. According to Hofmann this colour is that of compound No. 7, which is not formed in presence of strong acids. Sodium nitroprusside undergoes change in alkaline solution, the NO group being oxidised to NO$_2$. These reactions are formulated (see p. 681):
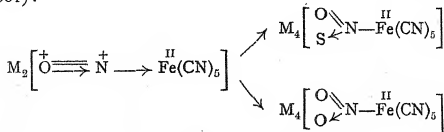
In weakly acid solution the reverse change occurs, and if carbon dioxide is passed through a solution of No. 6 compound it is converted into No. 1, with reduction of the NO_2. Compound No. 4, $[Fe(CN)_5(H_2O)]Na_3$, is formed when the NO group is removed with no neutral substance other than water available to take its place. The NO group is removed by reducing agents such as H_2S, hydroxylamine, phenylhydrazine, or by peroxides like H_2O_2 or PbO_2, but only at low temperatures; in warm solution hexacyanide compounds are formed.

The compound 2, containing ammonia, can be made by the action of gaseous ammonia (or a strong solution) on nitroprusside (1). If type 2 is treated with CO, type 3 results. On oxidation No. 2 gives the prussi-salt $[Fe^{III}(CN)_5(NH_3)]Na_2$ (No. 2a), which is the parent substance of the compound 4a, $[Fe^{III}(CN)_5(H_2O)]Na_2$. All these reactions are more or less reversible, and a pentacyanogen compound can even be converted into a hexacyanogen compound by excess of KCN. The compounds 5 and 8 can be made by the use of sodium arsenite and sulphite respectively; a prussi-salt is first formed, which is then reduced to prusso-salt, and the group SO_3 or AsO_2 then enters the complex.

The cobalt double cyanides give reactions similar to those of the iron compounds. Thus a gelatinous orange precipitate corresponding to prussian blue is formed when a solution of a soluble cobalt double cyanide is added to one of a cobalt salt. The cyanogen in these compounds can also be replaced by other radicals, but these substances have not been studied in detail.

Cobaltammines and Chromammines

The complex compounds in which ammonia functions as a neutral group are very numerous and frequently stable. Those of cobalt, chromium and gold are among the most important of the tervalent metals (for the ammines of the halides of the quadrivalent metals see p. 333) and have been frequently quoted in the preceding discussion; the halides of other tervalent metals form ammines, but they are not more stable than those of the bivalent metals (p. 270); to this class belong those of iron, aluminium and thallium. Ammines of tervalent vanadium and titanium have not yet been prepared.

The ammines of iron and aluminium halides are not formed at all in solution, for the affinity of these compounds for water is so much greater than that for ammonia that the ammines are at once converted into hydrates when wetted. The ammines can, however, be made in the dry way from the anhydrous halide and ammonia gas, when, like the halides of the bivalent metals (p. 270), the salts swell and absorb 6 mols. of ammonia. Aluminium iodide can take up more ammonia than this (up to 20 mols.), but this is not entirely due to formation of co-ordination compounds, being partly mere adsorption.[1] The

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[1] Franklin, *J. Amer. Chem. Soc.*, 1915, 37, 847.

ammonia is consequently mostly lost on heating, while the true ammines are fairly stable to heat; thus $AlCl_3.NH_3$ distils unchanged[1] at 400°. The ammines of tervalent Cr and Co decompose on heating, first giving off 1 mol. of NH_3 and then breaking down to the ammonium halide, nitrogen, and the bivalent halide of the metal. In solution, the complexes of these metals are very stable. They usually contain the maximum quantity of ammonia (6 mols.), and resemble the ammines of tervalent gold in behaviour. The gold ammines contain 4 mols. of ammonia as a maximum, and the complex ion is $[Au(NH_3)_4]^{\cdots}$; ammonia cannot be removed from them even by the strongest acids any more than it can from the cobalt and chromammines.[2] The ammines of the gold halides are subject to a peculiar decomposition like fulminating gold, which is discussed on p. 467.

Although most of the halide ammines are more easily made by the dry method mentioned above than by the use of ammonia in solution, it is curious to note that those which are most stable when produced are not prepared in the dry way. Anhydrous chromium chloride reacts with ammonia gas with great difficulty, and it is possible that the same steric hindrance which prevents its easy removal also prevents the entry of NH_3 into the molecule. Co-ordinated ammonia can be removed only when a part of the acidic residue outside the complex goes with it. In solution the particles are separated into ions, and the entrance of ammonia becomes easier; the insertion of neutral bodies is especially facilitated in liquid ammonia. The tervalent complexes $[Co(NH_3)_6]^{\cdots}$ and $[Cr(NH_3)_6]^{\cdots}$ are then formed, but the replacement of the halogen is not complete, and the complexes $[Co(NH_3)_5Cl]^{\cdots}$ and $[Cr(NH_3)_5Cl]^{\cdots}$ are also left in smaller quantity. Compounds containing these complexes are readily formed by oxidation of the ammines of the next lower halide; thus when chromous or cobaltous halides are dissolved in ammonia the complexes $[Cr(NH_3)_6]^{\cdot\cdot}$ and $[Co(NH_3)_6]^{\cdot\cdot}$ are formed, which pass into the ammines of the tervalent metals, the Cr compound spontaneously with evolution of hydrogen, and the Co compound when air is bubbled through the solution.

It is remarkable that the colours of the ammines are largely independent of the nature of the central atom. The compounds with $6NH_3$ (hexammines) are yellow—luteo-salts; the chloropentammines $[M(NH_3)_5Cl]^{\cdot\cdot}$ are purple-red—purpureo-salts; the brompentammines $[M(NH_3)_5Br]^{\cdot\cdot}$ are bluish violet; the compounds $[M(NH_3)_5H_2O]^{\cdots}$ (roseo-salts) are pink in all cases, whether the central atom is cobalt or chromium. The colour is in fact determined by the groups surrounding the metal atom.

The ammines of the metallic halides are the most characteristic and the most easily formed of all the ammines. The complexes are mostly studied as their halogen

[1] Baud, *Ann. Chim. Phys.*, 1904 (8), 1, 8.
[2] Weitz, *Ann.*, 1915, 410, 132.

derivatives or as nitrates, so that it is logical to deal with the ammines in general at this point with the occasional introduction of non-halogen compounds to make the discussion more complete. In the sequel, neutral groups will be indicated by A, acid radicals by X when outside the complex and by Y when within, while (en) indicates ethylenediamine, (pn) propylenediamine, (py) pyridine and (dipy) dipyridyl.

Complexes with SIX neutral groups, $[MA_6]X_3$

These complexes form tervalent cations; the most important forms are:

Chromammines:

$$[Cr(NH_3)_6]X_3 \qquad [Cr(en)_3]X_3 \qquad [Cr(pn)_3]X_3 \qquad [Cr(Urea)_6]X_3$$

Cobaltammines:

$$[Co(NH_3)_6]X_3 \qquad [Co(NH_2OH)_6]X_3 \qquad [Co(en)_3]X_3 \qquad [Co(pn)_3]X_3 \qquad [Co(dipy)_3]X_3$$

Luteo-salts.

Chromammines:

$$\left[Cr^{(NH_3)_5}_{H_2O}\right]X_3 \quad \left[Cr^{(NH_3)_4}_{(H_2O)_2}\right]X_3 \quad \left[Cr^{(en)_2}_{(H_2O)_2}\right]X_3 \quad \left[Cr^{(NH_3)_3}_{(H_2O)_3}\right]X_3 \quad \left[Cr^{(NH_3)_2}_{(H_2O)_4}\right]X_3 \quad \left[Cr^{py_2}_{(H_2O)_4}\right]X_3$$

Cobaltammines:

$$\left[Co^{(NH_3)_5}_{H_2O}\right]X_3; \qquad \left[Co^{(NH_3)_4}_{(H_2O)_2}\right]X_3 \qquad \left[Co^{(NH_3)}_{(H_2O)_3}\right]X_3$$
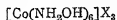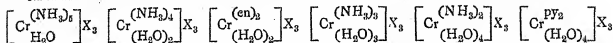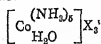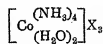
Roseo-salts. Diaquoroseo-salts
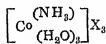
The luteo-salts are formed by the oxidation of the bivalent compounds in ammoniacal solution, as mentioned in the previous paragraph. They are always mixed with other halide ammines when made in this way, and the well-known phenomenon of ammoniacal solutions of cobalt chloride turning brown in the air involves the formation of the red $\left[Co^{(NH_3)_5}_{Cl}\right]Cl_2$ (purpureo-salt), green $\left[Co^{(NH_3)_4}_{Cl_2}\right]Cl$, the substance $\left[Co^{(NH_3)_3}_{Cl_2}H_2O\right]Cl$, and polynuclear types, e.g. $[Co_2O_2(NH_3)_{10}]X_4$, together with many other products besides the luteo-salt. When anhydrous chromic chloride is treated with liquid ammonia the compound $[Cr(NH_3)_6]Cl_3$ is produced (p. 311), but this method cannot be applied to the formation of the corresponding cobalt compound, as the cobaltic chloride is not known in the free state. Finally, the luteo-salts are formed by replacing acid radicals in a nucleus by ammonia—a method which has wide applications in the preparation of other ammines. For example, if the compound $\left[Co^{(NH_3)_5}_{Cl}\right]Cl_2$ is treated with a mixture of ammonia and ammonium chloride under pressure the ammonia replaces the Cl in the complex, the Cl passes into the outer sphere. The same effect is observed when there are several acid residues in the complex, and neutral groups can also replace one another. Thus compounds containing the groups $(en)_3$, $(pn)_3$, $(NH_2OH)_6$ can be prepared

by treating compounds containing ammonia and halogen in the nucleus with the substance it is desired to introduce. Thus one can make

$[Co(en)_3]Cl_3$ by heating $\left[Co\begin{smallmatrix}(NH_3)_5\\Cl\end{smallmatrix}\right]Cl_2$ with   ethylenediamine,

$[Cr(pn)_3]Cl_3$ „ „   „   „   propylenediamine,

$[Co(NH_2OH)_6]Cl_3$ „ „ $[Co(en)_3]Cl_3$ „ NH_2OH,

$[Cr(pn)_3]Cl_3$ „ „ $\left[Cr\begin{smallmatrix}Cl_3\\py_3\end{smallmatrix}\right]$ „   propylenediamine.
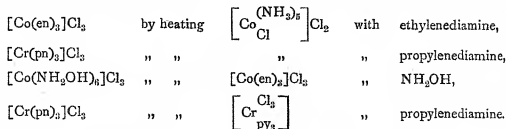
It might be expected that water would enter the nucleus under these conditions, as the reactions are carried out in aqueous solution but this does not occur in the ammines of tervalent Co and Cr, though it does happen with the ammines of other metals. There is, in these, a tendency for the hydrates of the salts to be formed, and only under exceptional conditions can the water be replaced by other groups in the nucleus. In the Co and Cr compounds, however, the neutral substances and negative radicals do not go into aqueous solution from the nucleus as long as the solution contains a small excess of the neutral group.

Water can, however, be introduced into the nuclei by acting on the ammines of Co and Cr with dilute acids. (Concentrated acids often give a different result ; the original salt is frequently precipitated, being insoluble in the acid.) It is sometimes sufficient to dissolve the ammine in the dilute acid, but with other compounds it is necessary to let the solution stand in the cold. In this way one obtains

$\left[Co\begin{smallmatrix}(NH_3)_4\\(H_2O)_2\end{smallmatrix}\right]X_3$ from $\left[Co\begin{smallmatrix}(NH_3)_4\\CO_3\end{smallmatrix}\right]X$; $\left[Co\begin{smallmatrix}(NH_3)_3\\(H_2O)_3\end{smallmatrix}\right]X_3$ from $\left[Co\begin{smallmatrix}(NH_3)_3\\(NO_3)_3\end{smallmatrix}\right]$;

$\left[Cr\begin{smallmatrix}(NH_3)_4\\(H_2O)_2\end{smallmatrix}\right]X_3$ „ $\left[Cr\begin{smallmatrix}(NH_3)_4\\H_2O\\(OH)\end{smallmatrix}\right]X_2$; $\left[Cr\begin{smallmatrix}(NH_3)_3\\(H_2O)_3\end{smallmatrix}\right]X_3$ „ $\left[Cr\begin{smallmatrix}(NH_3)_3\\(H_2O)_2\\(OH)\end{smallmatrix}\right]X_2$;

$\left[Cr\begin{smallmatrix}en_2\\(H_2O)_2\end{smallmatrix}\right]X_3$ „ $\left[Cr\begin{smallmatrix}en_2\\H_2O\\(OH)\end{smallmatrix}\right]X_2$; $\left[Cr\begin{smallmatrix}NH_3 \text{ or } py_2\\(H_2O)_4\end{smallmatrix}\right]X_3$ „ $\left[Cr\begin{smallmatrix}(NH_3)_2 \text{ or } py_2\\(H_2O)_2\\(OH)_2\end{smallmatrix}\right]X$.

Some of the compounds containing water must be prepared in a different way. Thus the ammines $[Co(NH_3)_5(H_2O)]X_3$ and $[Cr(NH_3)_5(H_2O)]X_3$ are made from $[M(NH_3)_5Cl]X_2$; the Co compound by the action of dilute ammonia, while the Cr compound gives with silver oxide an intermediate product, probably $[M(NH_3)_5(OH)]X_2$, which yields $[M(NH_3)_5(H_2O)]X_3$ when treated with dilute acids.

The hexa-urea-chromammine is made by treating urea with chromyl chloride, CrO_2Cl_2, when the chromium is reduced to the tervalent condition.

The salts of this class are isolated from their solutions by precipitation with concentrated acids, in which they are usually insoluble. A few are precipitated as nitrates, many as chlorides, although the bromides and iodides are more conveniently separated as they are less soluble than the chlorides. The anion of the salt obtained is that of the acid used for precipitation ; e.g. $[Co(NH_3)_6]Cl_3$ gives $[Co(NH_3)_6](NO_3)_3$ when precipitated with nitric acid.

The insolubility of the salts increases as the anion becomes larger. Hence complex anions give the least soluble salts and crystalline precipitates of the salts of the ammine cations with the anions $PtCl_6''$, $PtBr_6''$, $HgCl_4''$, HgI_4'', $Fe(CN)_6'''$, $Co(NO_3)_6'''$, BiI_4', I_3', etc., are readily obtained. The double compounds with 3 mols. $HgCl_2$ crystallise well and are characteristic for many of these ammines.

The colour of the hexammine salts is yellow to leather brown, in some approaching orange; the introduction of (en), (pn) or NH_2OH into the molecule does not alter the colour much, but when H_2O occupies some of the co-ordination positions the colour is redder (roseo-salts), and compounds with $3H_2O$ are quite dark red.

Complexes with FIVE neutral groups, $\left[M^{A_5}_Y\right]X_2$ and $\left[M^{A_5}_Y\right]X$

These complexes are bivalent cations when the radical Y is that of a monobasic acid, thus, $[Co(NH_3)_5Cl]^{\cdot\cdot}$, but they become univalent when the radical of a dibasic acid is present in the nucleus, e.g. $[Co(NH_3)_5(SO_4)]^{\cdot}$. The properties of the two classes of compounds are not very different. The most important substances in this group are:

Chromammines: $\left[Cr^{(NH_3)_5}_Y\right]X_2 \quad \left[Cr^{(NH_3)_4}_{H_2O}{}_Y\right]X_2 \quad \left[Cr^{(NH_3)_3}_{(H_2O)_2}{}_{(OH)}\right]X_2 \quad \left[Cr^{(NH_3)_2}_{(H_2O)_3}{}_{(OH)}\right]X_2$

Y=Cl, Br, I, CNS,   X=Cl, Br, I,
NO_3, NO_2, (OH),   (OH)

Cobaltammines: $\left[Co^{(NH_3)_5}_Y\right]X_2 \quad \left[Co^{(NH_3)_4}_{H_2O}{}_Y\right]X_2 \quad \left[Co^{(NH_3)_3}_{(H_2O)_2}{}_{Cl}\right]X_2 \quad \left[Co^{(NH_3)_2}_{(H_2O)_3}{}_{Cl}\right]X_2$

Y = Cl, Br, I, CNS,   Y = NO_2, NO_3,
NO_3, NO_2 Cl, Br, CN

and a few with Y a bivalent radical: $\left[Cr^{(H_2O)_5}_{SO_4}\right]X \quad$ and $\quad \left[Co^{(NH_3)_5}_Y\right]X$

Y = SO_3, SO_4, CO_3, C_2O_4.
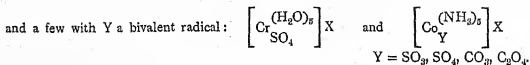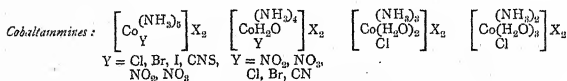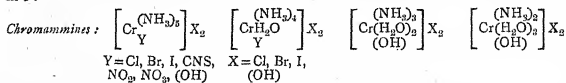
Some similar compounds have been prepared with (py), (en), NH_2OH, etc., as neutral groups.

The first group of these compounds is the most important, and owing to the prevalent purple-red to violet colour they are known as the purpureo-salts. The iodine compounds are, however, green, and those which contain NO_2 are pale yellow (xantho-salts), while the nitrato-chromium compounds are intermediate in colour—a pale flesh pink.

These substances are prepared by the methods used for the hexammine series. By gentle heating one of the neutral groups can be expelled from a compound which contains six of them, and when this happens an acid radical from the outer sphere enters the complex, giving a nucleus of the type now under discussion. The following reactions are examples of this:

$$\left[Co(NH_3)_6\right]Cl_3 \xrightarrow{-NH_3} \left[Co^{(NH_3)_5}_{Cl}\right]Cl_2,$$

$$\left[Co^{(NH_3)_5}_{H_2O}\right](NO_3)_3 \xrightarrow{-H_2O} \left[Co^{(NH_3)_5}_{(NO_3)}\right](NO_3)_2.$$
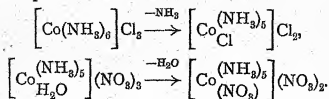
The usual method of preparing compounds of this group containing cobalt is to digest the compound $[Co(NH_3)_5(H_2O)]X_3$ for a long time with the acid whose negative ion it is desired to introduce into the nucleus ; *e.g.* :

$$\left[Co\begin{matrix}(NH_3)_5\\H_2O\end{matrix}\right]X_3 + 3HBr = \left[Co\begin{matrix}(NH_3)_5\\Br\end{matrix}\right]Br_2 + 3HX + H_2O.$$
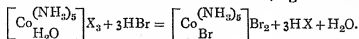
The salts formed in this way always have the same acid radical inside and outside the complex—chlorochlorides, thiocyanato-thiocyanates, oxalato-oxalates, etc., are formed. When treated with other acids the ionic radical inside the complex remains, while the ion in the outer sphere is replaced. Thus treatment of bromobromides or oxalato-oxalates with hydrochloric acid results in the formation of bromochlorides or oxalatochlorides respectively. The compound $[Co(NH_3)_5H_2O)]X_3$, which is used as a starting-point for the preparation, need not be pure. It is one of the main products of the oxidation of ammoniacal cobalt solutions in the air, and the oxidation is allowed to go on in presence of the ammonium salt of the anion which it is desired to introduce into the nucleus. Boiling with the acid completes the preparation. For example, to make $[Co(NH_3)_5Cl]Cl_2$ an ammoniacal cobalt solution containing ammonium chloride is oxidised in the air and then boiled with hydrochloric acid. The insolubility of the purpureo-salts in water (and they are even less soluble in the presence of acids) permits of their separation from other ammines. When they contain one of the complex anions mentioned as useful for the isolation of the luteo-salts (p. 311), the salts are particularly insoluble.

The chromo - purpureo - salts are similarly prepared, but the compound $[Cr(NH_3)_5(H_2O)]X_3$ is not so easily obtained as the corresponding Co compound, so pentammine compounds which have another group in place of H_2O are used. The chloro- and bromo-compounds are made by boiling the hexammine derivatives with HCl or HBr, the thiocyanato-complexes by boiling with HCNS, and so on. Complexes containing the OH group are made by treating the aquo-pentammine salts with dilute ammonia ; it is not necessary to carry out this reaction in acid solution, as the mere presence of the ion is sufficient to ensure that it is introduced.

All the other groups of this series contain water as one of the neutral substances in the nucleus. Their colour is not much altered by this difference in composition, though they are somewhat redder than the pentammine salts. They are for the most part very insoluble in water.

The principle of the method of preparing them is the same as that used for the pentammines. On boiling a cobalt compound containing ammonia and halogen in the nucleus with slightly acidified water, the water takes the place of the halogen; *e.g.* :

$$\left[\begin{matrix}(NH_3)_4\\CoCl\\NO_2\end{matrix}\right]X \xrightarrow{+H_2O} \left[\begin{matrix}(NH_3)_4\\CoH_2O\\NO_2\end{matrix}\right]X_2 \qquad \left[\begin{matrix}(NH_3)_4\\CoBr\\Br\end{matrix}\right]X \xrightarrow{+H_2O} \left[\begin{matrix}(NH_3)_4\\CoH_2O\\Br\end{matrix}\right]X_2$$

$$\left[\begin{matrix}(NH_3)_5\\CoCl_2\end{matrix}\right]X \xrightarrow{+H_2O} \left[\begin{matrix}(NH_3)_3\\Co(H_2O)_2\\Cl\end{matrix}\right]X_2 \qquad \left[\begin{matrix}(NH_3)_2\\Co(H_2O)_2\\Cl_2\end{matrix}\right]X \xrightarrow{+H_2O} \left[\begin{matrix}(NH_3)_2\\Co(H_2O)_3\\Cl\end{matrix}\right]X_2$$
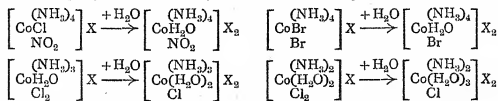
The deep red chromium compounds are prepared by the reverse reaction. Starting with a compound containing more water, a portion of the water is removed on precipitation with concentrated acid in the presence of ammonium salts, and the anion of the acid enters the nucleus. Thus $\left[Cr\begin{matrix}(NH_3)_2\\(H_2O)_4\end{matrix}\right]Cl_3$ with conc. $HCl + NH_4Cl$ gives

$\left[\begin{matrix}(NH_3)_4\\CrH_2O\\Cl\end{matrix}\right]Cl_2$. The original compound is made by precipitating chrome alum

with ammonia and dissolving the ppt. in an ammoniacal solution of an ammonium salt. In these complexes the acid radical can be replaced by OH if a little pyridine is added.

Complexes with FOUR neutral groups

There are many different types of compounds in this class. When the two acid radicals are each univalent, or when these positions are occupied by a single bivalent radical, the whole complex is a univalent cation ; e.g.:

$$\left[Co(NH_3)_4(\overset{2\times I}{CNS})_2\right]^{\cdot} \qquad \text{or} \qquad \left[Co(NH_3)_4\overset{II}{CO_3}\right]^{\cdot}.$$
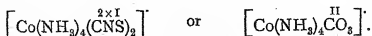
If one of the ionic groups is uni- and the other bivalent, the complex is a non-ionised compound and is electrically neutral ; e.g. $\left[Co(NH_3)_4(\overset{I}{NO_2})(\overset{II}{SO_4})\right]$. Finally, when both the radicals are bivalent the complex is a univalent anion ; e.g. $\left[Co(NH_3)_4(\overset{2\times II}{SO_4})_2\right]'$ which may be regarded as $M\left[Co\overset{(NH_3)_4}{}\left(O\!\!-\!\!\overset{}{}\!\!-SO_2\!\!-O\right)_2\right]$ (cf. p. 290).
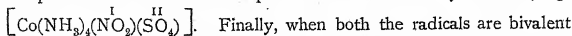
The variety of compounds which compose this class is still further increased by the possibility of the existence of cis and trans forms (see p. 295), which differ in colour and reactions. In the classes discussed so far there has been a fair uniformity of colour, but in this one the greatest variety exists, and besides light yellow and brown compounds there are green, violet, reddish, deep red and blue ones. The colour of the corresponding Co and Cr compounds is again very similar. In this treatment those compounds which are most important or best known will be selected ; the methods of preparation do not as a rule differ from those described for the previous groups.

The compounds $\left[Co\overset{(NH_3)_4}{(NO_2)_2}\right]X$ occur in two stereoisomeric forms, both brownish yellow in colour. The cis forms are known as flavo-salts, the trans forms as croceo-salts. The constitution of the cis compounds is fixed by their preparation from carbonato-compounds (see below) but inversion is not excluded ; the trans forms are prepared by exposing solutions of cobaltous salts containing ammonia and nitrite to atmospheric oxidation. When potassium cobaltinitrite is treated with ethylenediamine both cis and trans forms of the compound $[Co(en)_2(NO_2)_2]X$ are formed.

The compounds $\left[Co\overset{(NH_3)_4}{Cl_2}\right]X$ are distinguished by the different colours of the isomers. The cis salts made from $[Co(NH_3)_4CO_3]X$ are violet and hence called violeo-salts. They are, however, rapidly changed into the green trans form, the praseo-salts—sometimes so rapidly that the violet salt cannot be isolated. The compounds which contain (en) or (py) in place of NH_3 are more stable in the cis condition.

The radicals Br and CNS, or even two different ones, can replace the Cl, and the corresponding chromammines are similar.

$RuCl_3$ with aqueous ammonia gives "ruthenium red"[1] which has been shown by Morgan and Burstall[2] to be $\left[\begin{array}{c}HO\\Cl\end{array}\!\!>\!\!Ru(NH_3)_4\right]Cl$, forming with HCl, $[Ru(NH_3)_4Cl_2]Cl.2H_2O$, with HBr, $[Ru(NH_3)_4Br(OH)]Br.H_2O$, and with HNO_3, $[Ru(NH_3)_4Cl(NO_3)]NO_3.4H_2O$. K. Gleu and his co-workers have recently prepared a large number of ruthenium ammines.

Salts of formula $\left[Co\!\!\begin{array}{c}(NH_3)_3\\(H_2O)\\Cl_2\end{array}\right]X$ show dichroism and are sometimes referred to as the dichro-salts. Besides the blue form there is a deep-green variety, which in large crystals appears black but is dark red by transmitted light. This compound is formed if, after oxidation in the air, the excess of ammonia is removed by evaporation and the liquid treated with conc. hydrochloric acid.

The formation of the compound $\left[Co\!\!\begin{array}{c}(NH_3)_2\\(H_2O)_2\\Cl_2\end{array}\right]X$ is a good example of the way complex anions can be converted into cations. It is formed when the anionic complex compound $\left[Co\!\!\begin{array}{c}(NH_3)_2\\(NO_2)_4\end{array}\right]K$ is treated with conc. hydrochloric acid. Two of the nitrite groups are replaced by Cl, the other two by water, a univalent positive complex being the result. The carbonato-tetrammine compound $\left[Co\!\!\begin{array}{c}(NH_3)_4\\CO_3\end{array}\right]X$ is the most important of those which have a bivalent acid radical in the nucleus, as it is the starting-point for the preparation of many cobaltammines. It is easily prepared by the oxidation of cobalt solutions containing ammonia and ammonium carbonate by atmospheric oxygen. Its deep carmine lamellae are much more soluble than the purpureo-salts of similar colour, and indeed the whole group is distinguished from the classes previously considered by greater solubility. The carbonato-group is easily replaced on treatment with acids, and it is remarkable that the carbonato-compound gives compounds with an anionic complex with acid salts. Thus, when treated with an acid sulphite, two sulphite radicals enter the complex and the compound $\left[Co\!\!\begin{array}{c}(NH_3)_4\\(SO_3)_2\end{array}\right]M$ is formed, the brown cis salt and the reddish-yellow trans salt being formed simultaneously.

The chromium compounds of this class are in general similar to those of cobalt. The halogen radical is, however, easily exchanged

[1] *Compt. rend.*, 1892, 114, 291 ; 115, 1299.
[2] *J. Chem. Soc.*, 1936, 41.

for the OH group in these compounds, a reaction which does not obtain in the Co complexes, as already remarked when the chrom-purpureo-salts were discussed. Thus, when the di-brom-salt (I) is treated with pyridine, the lilac dihydroxo-salt (II) is formed:

$$\text{I.} \quad \left[\text{Cr} \begin{matrix} (NH_3)_2 \\ (H_2O)_2 \\ (Br)_2 \end{matrix} \right] X. \qquad \text{II.} \quad \left[\text{Cr} \begin{matrix} (NH_3)_2 \\ (H_2O)_2 \\ (OH)_2 \end{matrix} \right] X.$$

Other neutral groups can take the place of the ammonia. When the green hydrate of chromium chloride is treated with pyridine, a grey-green di-pyridino-compound corresponding to substance (II) above is obtained by the replacement of two Cl atoms by pyridine and of two water molecules by OH groups.

Complexes with THREE neutral groups

In these compounds there are, besides the three neutral groups, three univalent radicals or their equivalent, the three valencies of the central metal itself being thus neutralised, so that the whole complex is electrically neutral. The compounds in consequence show no tendency to form salts, and they are remarkably insoluble. The ammines of cobalt of this class which are best known are those of the types $[Co(NH_3)_3Y^I_3]$ and $[Co(NH_3)_3Y^IY^{II}]$, the most important being $\left[Co \begin{matrix} (NH_3)_3 \\ (NO_2)_3 \end{matrix} \right]$; this on being heated[1] with aqueous $NaBO_2$ gives $Na_3[Co(BO_2)_3NH_3]$. The chromium complexes are similar, and may also contain pyridine, thiourea and water. Cl, NO_3, NO_2, SO_4, etc., are the typical acid radicals in the cobalt compounds; those containing the nitrite group are yellow and the other compounds are violet; with both nitrite and another acid present, the colour is intermediate. The methods of preparation are similar in principle to those used for types of compounds previously discussed. Hofmann and Wiede[2] prepared an important series of compounds of this class which contain sulphur directly united to the cobalt atom. One of these, $\left[\begin{matrix} (NH_3)_3 \\ CS_3 \end{matrix} Co\text{-}S\text{-}Co \begin{matrix} (NH_3)_3 \\ CS_3 \end{matrix} \right]$, is formed when freshly precipitated cobalt hydroxide is warmed with ammonia and carbon disulphide. They range from dark brown to black in colour.

Complexes with TWO neutral groups

Few substances of this class have been prepared; of the chromium salts only thio-, cyanato- and oxalato-compounds are known; of the cobalt salts, only those with nitrite and oxalate radicals in the complex.

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[1] Duval, Compt. rend., 1929, 188, 176.
[2] Z. anorg. Chem., 1897, 14, 263.

Only ammonia functions as neutral group in the cobalt salts, but chromium salts containing also water, pyridine and ethylenediamine are known. The complex is a univalent anion of general formula $\left(M\begin{smallmatrix}(NH_3)_2\\Y_4\end{smallmatrix}\right)'$. The salts crystallise well, those of Cr having colours orange to red, while those of Co are reddish brown. The complex anion is so large that the cations combined with it effect a balancing by attaching to themselves a number of neutral groups (*cf.* p. 301). The salts of the complex with heavy metals combine with large quantities of ammonia, and even the alkali metal salts, in which the property is seldom found, combine with neutral groups; for instance, the compound $[Cr(py)_2(CNS)_4]K$ can add to itself 4 mols. of pyridine.

The most important cobaltammine of this class is the compound $\left[Co\begin{smallmatrix}(NH_3)_2\\(NO_2)_4\end{smallmatrix}\right]NH_4$, Erdmann's salt,[1] which yields characteristic salts with cations of large volume owing to its voluminous anion. It can therefore be used to characterise and precipitate complex cations. Thus ions like $\left[Cr\begin{smallmatrix}(H_2O)_4\\Cl_2\end{smallmatrix}\right]$ and $\left[CoH_2O\begin{smallmatrix}(NH_3)_3\\Cl_2\end{smallmatrix}\right]$ give very stable precipitates. The reagent itself is made by allowing neutral solutions of bivalent cobalt to stand after addition of ammonium salts and nitrite.

The best known of these chromammines is Reinecke's salt, $\left[Cr\begin{smallmatrix}(NH_3)_2\\(CNS)_4\end{smallmatrix}\right]NH_4, H_2O$, probably the only metal ammine which is formed by a fusion process.[2] This beautiful red salt is produced when ammonium thiocyanate is melted and ammonium dichromate added. In the complicated reaction which ensues, Morland's salt, the guanidinium salt of the same complex, is formed in considerable quantities as a by-product. The free acid $\left[Cr\begin{smallmatrix}(NH_3)_2\\(CNS)_4\end{smallmatrix}\right]H$ can also be obtained in red scales by decomposing the barium salt in solution with sulphuric acid and then evaporating or extracting with ether. The tendency for acids with an anion of large volume to form additive compounds with ether has already been noted (p. 305; *cf.* p. 507).

Complexes with ONE neutral group

No cobalt salts of this kind are known, and no ammines of chromium salts. The aquo-salts of the type $\left[Cr\begin{smallmatrix}(H_2O)\\Y_5\end{smallmatrix}\right]M_2$, in which Y can be F, Cl, Br, have already been discussed as double halides (p. 303). The complex is bivalent.

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[1] *J. prakt. Chem.*, 1866, **97**, 410.
[2] See *Organic Syntheses*, 1935, **15**, 74.

Complexes without neutral groups

These are of the general type $[CrX_6]M_3$, and include the anhydrous double halides and oxalates of chromium: $[CrF_6]M_3$, $[Cr(CN)_6]M_3$, $Cr(CNS)_6]M_3$, $[Cr(C_2O_4)_3]M_3$, etc., as also some cobalt salts, such as the well-known cobaltinitrites $[Co(NO_2)_6]M_3$. The yellow alkali salts of the latter complex are obtained on treating a solution of a cobaltous salt with alkali nitrite in presence of acetic acid; the potassium salt (Fischer's salt) is particularly insoluble, and is used for the quantitative determination of potassium. The sodium salt is much more soluble. Complexes of this type, in contrast with the ammine complexes, are not confined to cobalt and chromium, but are common to all tervalent metals.

Multinucleate Ammines

In the complexes so far discussed only one metal atom is found in the nucleus. There are, however, many complexes in which several metal atoms are joined to negative radicals in a non-ionisable manner. To this class belong the polymerised metallic halides, such as Al_2Cl_6 (p. 275), but in most of these the complex is easily broken up. Molybdenum dichloride, Mo_3Cl_6, is a stronger complex (p. 265) and can be given the formula $[Mo_3Cl_4]Cl_2$, for two of the acid radicals are particularly prone to replacement by OH groups or by other acid radicals,

$$i.e. \left[Mo \underset{Cl}{\overset{Cl}{<}} Mo \underset{Cl}{\overset{Cl}{<}} Mo \right] Cl_2$$
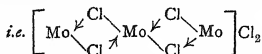
Diethylauric bromide is dimeric in benzene solution and is formulated[1]:

$$\begin{array}{cc}
C_2H_5 & C_2H_5 \\
{}_{C_2H_5}{>}Au \underset{Br}{\overset{Br}{<}} Au {<}_{C_2H_5} & \text{and AuCN is}
\end{array}
\qquad
\begin{array}{c}
Au—C{\equiv}N \to Au \\
\uparrow \qquad | \\
N \qquad C \\
{\parallel} \qquad {\parallel} \\
C \qquad N \\
| \qquad \downarrow \\
Au \leftarrow N{\equiv}C — Au
\end{array}$$
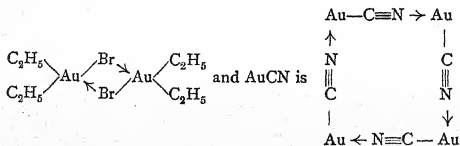
The multinucleate ammines, especially those of Co and Cr, have been more closely investigated than these chlorides.

The metal atoms in multinucleate ammines are joined by an atom or group which forms a bridge. Two examples of binucleate ammines are:

$$[(NH_3)_5Co—NH_2 \longrightarrow Co(NH_3)_5]X_5 \quad \text{and} \quad [(NH_3)_5Cr—O—Cr(NH_3)_5]X_4.$$
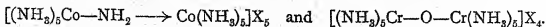
In the first, one of the links between the Co and NH$_2$ group is covalent, the other the semi-polar (i.e. co-ordinate) type; in the Cr compound both the oxygen bonds are covalencies.

The bridge can be formed by the groups NH$_2$, OH, O, O$_2$, NO$_2$, SO$_4$, etc., but two metal atoms can be joined together by as many

[1] Gibson and Simonsen, J. Chem. Soc., 1930, 2531; Gibson, Nature, 1937, 140, 583.

as three bridges, since the two octahedra can at the most each have a face in common (*i.e.* three corners of each). The following are examples of compounds with several bridge groups:

$$\left[en_2Co \underset{NH_2}{\overset{O-O}{<}} Co\ en_2 \right] X_3 \qquad \left[(NH_3)_3Co \overset{NH_2}{\underset{\underset{H}{O}}{\overset{\underset{H}{O}}{<}}} Co(NH_3)_3 \right] X_3$$
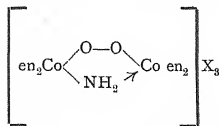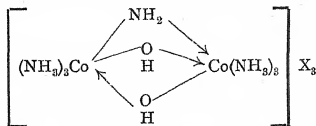
Two-bridge groups.   Three-bridge groups.

Finally, more than two nuclei can be joined together by bridges, as in the ternucleate compound:

$$\left[(NH_3)_3Co \overset{\underset{H}{\overset{H}{O}}}{\underset{\underset{H}{O}}{<}} Co \underset{\underset{H}{O}}{\overset{\overset{H}{O}}{<}} Co(NH_3)_3 \right] X_3.$$
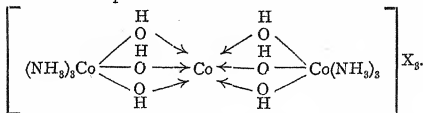
The simplest and most easily obtained of the multinucleate cobalt-ammines are the peroxo-salts $[(NH_3)_5Co—O—O—Co(NH_3)_5]X_4$, which are formed when ammoniacal solutions of cobaltous salts containing ammonium salts absorb molecular oxygen from the atmosphere. The melano-salts are made in a similar way:

$$\left[\overset{(NH_3)_3}{\underset{X_2}{}}Co—NH—Co\overset{(NH_3)_3}{\underset{X_2}{}} \right],$$
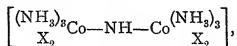
having the imido-group in place of oxygen. These and analogous compounds have a distinctive dark colour, almost black, but in thinner layers they appear dark brown to olive green.

The chrommammines with an OH bridge are the best known; they are red to carmine in colour. The simplest, the so-called rhodo-salts
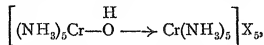
$$\left[(NH_3)_5Cr—O\overset{H}{\longrightarrow} Cr(NH_3)_5 \right]X_5,$$

are prepared in a similar way to the cobalt peroxo-salts above. These compounds have a neutral reaction, but are isomeric with the erythro-salts $[(NH_3)_5Cr—O—Cr(NH_3)_5]X_4HX$ which have an acid reaction and may be regarded as analogous to the acid addition products of the ethers, *i.e.*:

$$\overline{X}_4 \left[\overset{(NH_3)_5\overset{++}{Cr}}{\underset{(NH_3)_5\overset{++}{Cr}}{}} \overset{+}{>} O \overset{H}{<} \right] \overline{X}.$$
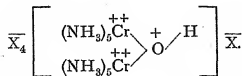
These two modes of formulation, however, seem scarcely distinguishable.

X

The erythro-salts are formed by precipitating their ammoniacal solution with dilute acid. The following rhodoso-salt has four nuclear atoms in its very complex major nucleus:

$$\left[Cr \left(\begin{array}{c} H \\ O \\ O \\ H \end{array} > Cr(NH_3)_4 \right)_3 \right] X_6.$$
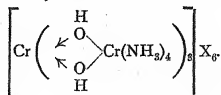
This substance is obtained instead of the hexammine $[Cr(NH_3)_6]X_3$ when a solution containing a chromic salt, an ammonium salt and ammonia is allowed to stand for a long time. The corresponding compound of Co was the first metallic complex to be resolved which did not contain carbon [1] ($[M] = \pm 47,500°$).

All these multinucleate chromammines pass into simple complexes when boiled for a long time with acids.

Many multinucleate compounds of Pt, Pd, Zn, Cd, Hg, Cu, and Ag have been described, halogens forming the "bridge" in most cases.[2]

For the complex compounds of platinum, see pp. 333, 337.

[1] Werner, *Compt. rend.*, 1914, 154, 426.
[2] Mann, *Ann. Rep. Chem. Soc.*, 1938, 35, 148

HALIDES OF QUADRI-, QUINQUE- AND SEXA-VALENT METALS

Halides of quadrivalent metals—Their complex compounds—Platinum ammines—(Ammines of bivalent platinum)—Internally complex compounds—Halides of quinque-, sexa-, and octa-valent metals

Halides of Quadrivalent Metals

Formation.—The formation of these halides seldom takes place in aqueous solution, as they are very easily hydrolysed. Dry methods are therefore used, as already described for the tervalent metals on p. 272. The action of the free halogen on the metals or their alloys, carbides, silicides, nitrides, etc., or that of a halide of a non-metal on the oxides, usually in the presence of carbon, are suitable methods.

Thus zirconium chloride is produced by heating the metal in chlorine or in hydrogen chloride, or by heating zirconium carbide in a current of chlorine. Starting with zirconium oxide, the chloride can be obtained by mixing the oxide with carbon and then passing over the red-hot mixture either chlorine itself or HCl, $SiCl_4$, CCl_4, BCl_3, PCl_5, S_2Cl_2, the last being used in conjunction with chlorine. Similar methods are applicable to the production of the bromide and iodide of this metal, as also to that of the tetrahalides of tin, thorium, titanium, vanadium and uranium. Tin tetrachloride is so easily made from the metal and chlorine that other methods are not used. When Cl_2 is passed over granulated tin warmed to a temperature below that at which it melts, the liquid is obtained practically free from chlorine. ₠· The reaction is more difficult to bring about when a noble metal is used; thus platinum is not much attacked by chlorine at a red heat unless the action is catalysed by non-metallic chlorides such as $AsCl_3$ or $SeCl_4$. Even fluorine does not attack platinum below a red heat.

As free fluorine is not easy to obtain, it is usual to decompose the chlorides with anhydrous HF (Ruff). In this way VF_4, ZrF_4, TiF_4 and SnF_4 can be obtained. In a somewhat similar way ZrF_4 can be made by heating ZrO_2 with CaF_2 or NH_4F, when the volatile ZrF_4 distils; GeF_4 can also be made by heating GeO_2 with CaF_2 and concentrated sulphuric acid (*cf.* SiF_4, p. 778), or by heating $BaGeF_6$.

The similarity between SiF_4 and GeF_4, which is to be expected from their adjacent positions in the Periodic Table, is also shown by the formation of derivatives containing hydrogen as well as halogen. Germanium tetrachloride is not produced when HCl

is passed over the metal, but the compound $GeHCl_3$ (b.pt. 75°), in the same way that silico-chloroform $SiHCl_3$ is formed by the action of HCl on silicon. Further, when GeF_4 is passed into water, the hydrolysis gives not only the oxide or hydroxide, but also H_2GeF_6 corresponding to hydrofluosilicic acid.

The less soluble of the halides of this class can be made by double decomposition. Thus SnI_4 is formed when KI is added to a solution of $SnCl_4$, and the very insoluble UF_4 is produced by the action of HF on uranium oxide, ThF_4 being made in a similar way.

The tetrahalides can often be made by heating other halides. $MoCl_3$ breaks up into $MoCl_2$ and $MoCl_4$ on heating, and WCl_4 is obtained when WCl_6 is reduced with hydrogen. Complex halides are also often easily decomposed. Thus when H_2PtCl_6 is carefully heated in a current of chlorine at 275° the tetrachloride is left. H_2PbCl_6 decomposes at the ordinary temperature in presence of concentrated sulphuric acid, and $PbCl_4$ is formed when $(NH_4)_2PbCl_6$ is stirred into the acid in the cold. It is curious that the fluoride cannot be made in a similar way, as it might be expected to be more stable than the chloride; it has not so far been prepared, though Ruff and Plato[1] have shown that it does not exist above 35°. The double fluoride, K_3HPbF_8, however, is known; on heating, it breaks up into HF and K_3PbF_7 at about 200°, the latter compound passing at higher temperatures to $3KF$, PbF_2 and F_2.

Only the chlorides and not the bromides or iodides are known in some instances, e.g. lead and vanadium. The tetrahalides of Mn and Ce are known only as double salts—derivatives of the complex acids H_2MnCl_6, etc. In general these halides are more stable as complexes, and even those which decompose fairly easily with liberation of halogen form complex acids of considerable stability, especially when the metal is one with non-metallic tendency, e.g.:

H_2MnCl_6	H_2PbCl_6	H_2SnCl_6	H_2PtCl_6
$HAuCl_4$	$HSbCl_6$	H_2TeCl_6	

Properties.—*Behaviour as Salts.*—With increase in valency the electropositive character of the metals diminishes, and, while those of intermediate valency have amphoteric properties, the metals which exhibit high valencies frequently give rise to acids. The properties of the quadrivalent halides are affected by this general consideration, and they are no longer true salts, for they show little tendency to ionise in aqueous solution, and even in the fused state they are not good conductors of electricity. The presence of ions in solutions of these halides can be demonstrated only in a few cases. Walden has shown that $SnCl_4$ is ionised in liquid sulphur dioxide, but the dissociation is very irregular and an indeterminate mixture of $SnCl_3{}^{·}$, $SnCl_2{}^{··}$, $SnCl{}^{···}$ and $Sn{}^{····}$ ions is formed. SnI_4 dissolved in $SbCl_3$ is a very poor conductor (cf. p. 234).

[1] Z. anorg. Chem., 1917, 98, 27.

Physical Properties and Molecular Weight.—These halides approach those of the non-metals in their physical properties, particularly in

		F_4	Cl_4	Br_4	I_4
Ge	Melting point . .	...	$-49.5°$	$26°$	$144°$
	Boiling point . .	$-104°$	$85.6°$	$183°$	$350-400°$
Sn	Melting point . .	...	$-33°$	$33°$	$143°$
	Boiling point . .	$705°$	$114°$	$203°$	$341°$
Pb	Melting point . .	...	$-15°$	...	...
Ti	Melting point . .	...	$-23°$	$40°$	$150°$
	Boiling point . .	$284°$	$136°$	$239°$	$360°$
V	Melting point . .	Decomp.	$< -18°$	...	...
	Boiling point . .	...	$154°$	...	...

being easily fusible. The tetrachlorides of Sn, Pb, Ti, Ge and V are liquid at the ordinary temperature; the melting points and boiling points are given in the table above.

The melting and boiling points of these compounds show some analogies with those of the inert gases; for the non-polar character of these compounds results in closed orbits for the electrons similar to those in these gases.[1] If the melting and boiling points of the halides of Si, Ge, Sn, Pb, Ti and B are plotted as ordinates, and those of the inert gases as abscissæ, straight lines are obtained by joining the points derived from the chlorides and argon, the bromides and krypton and the iodides and xenon, as in Figs. 50 and 51. Carlson states that in general the melting and boiling points of unassociated pseudo- and non-electrolytes are proportional to those of the corresponding rare gas. It is thus possible to calculate these constants for unknown compounds by this rule.

The halides of some metals in this group are, however, solid and of high melting point, *e.g.* those of W, U, Zr, Th and Pt. Zirconium fluoride sublimes only at a white heat, that of thorium melts at a red heat. Uranium iodide melts at 500°, $ThCl_4$ at 820°.

FIG. 50.—Connection between melting points of halides and of the inert gases.

[1] H. Carlson, *Ber.*, 1925, 58, 1747.

The high boiling point of the fluorides can be noticed in the above table; they are probably polymerised in the solid state, as is indicated by their insolubility. The other compounds of the group, in so far as their vapour densities have been determined, are unimolecular, and
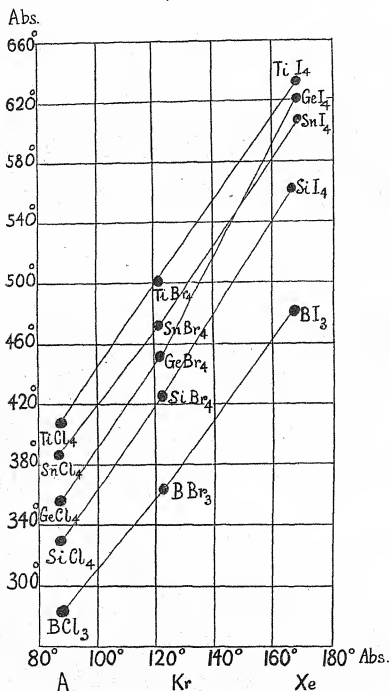
FIG. 51.—Connection between boiling points of halides and of the inert gases.

differ in this respect from the halides of the tervalent metals which are often bimolecular (*cf.* p. 274). The true densities of the vapours cannot always be found, as decomposition into lower halides occurs at higher temperatures. Many of them, however, show the normal density up to 1100° (*e.g.* ThCl₄), and decompose only at still more elevated temperatures. The Pt halides decompose readily, thus giving

a high vapour pressure, although they sublime unchanged to a slight extent. $PtCl_4$ decomposes in an atmosphere of Cl_2 into $PtCl_2$ and Cl_2 at 370°, and $PtCl_3$ and $PtCl$ exist over short ranges (p. 232), the bromide breaks down into $PtBr_2$ and Br_2 on drying in the air at 190°, and PtI_4 gives off iodine at the ordinary temperature. The iodides are the least stable of these halides.

Colour, etc.—The colour and appearance of the quadrivalent halides are shown in the following table:

	F_4	Cl_4	Br_4	I_4
Ti	Colourless powd.		Dark yellow cryst.	Dark red
Zr	Colourless cryst.		White powd.	Red-brown powd.
Th	White amorph. powd.	Colourless liq.	White	White
Ge	Colourless gas	White mass	White octahedra	Orange cryst. Vapour yellow
Sn	White cryst.		Snow-white cryst.	Red or yellow octahedra
Pb		Yellow oil		
V	Brown powd.	Reddish-brown liq.		
Mo		Brown powd. Vapour yellow	Black needles Vapour red	
W	...	Grey-brown cryst.		Black
U	Green powd.	Dark green octahedra Vapour red	Brown cryst.	Black cryst.
Pt	Dark red	Brown tables	Dark brown amorph.	Black amorph.

Hydrolysis.—These halides are the salts of very weak bases and are consequently extensively hydrolysed in aqueous solution; the hydrolysis of tervalent halides is considerable, but in the quadrivalent state it is greater still. The ease with which water decomposes these halides is shown by the way in which many of them fume in the air, *e.g.* those of Ge, Sn, Ti, Zr, V, etc.—$SnCl_4$ was called "spiritus fumans Libavii" by the later alchemists. The fuming is due to the formation of the gaseous halogen acid. On adding these compounds to water, decomposition ensues with evolution of heat, and is often accompanied by a hissing sound (*e.g.* $ThCl_4$, $MoCl_4$, SnF_4, UBr_4, etc.). Further, many of them are hygroscopic, and, when solid, deliquesce in the air; the polymerised fluorides are exceptional in dissolving but slightly in water, but the dissolved portion is rapidly hydrolysed (UF_4, ZrF_4, SnI_4 and WI_4).

The extent of hydrolysis is variable. Some of the halides of this group are completely decomposed and give precipitates of oxide or hydroxide; thus germanium chloride yields crystalline germanium dioxide when treated with water. But as a rule clear solutions are first obtained and the hydrolysis is gradual, and intermediate compounds are frequently formed, some of which have been isolated. They are addition compounds with water, which break up with liberation of the halogen acid. Thus tin tetrachloride dissolves in water to a clear

solution (like SnF_4, $SnBr_4$ and the halides of Ti, Zr, V, U), but after a time the hydroxide separates. According to Pfeiffer,[1] an aquo-compound is first formed, which yields the hydroxide and the halogen acid on subsequent decomposition

$$Sn \begin{matrix} Cl_4 \\ (H_2O)_x \end{matrix} \xrightarrow[]{-HCl} Sn \begin{matrix} Cl_3 \\ (OH) \\ (H_2O)_{x-1} \end{matrix}$$
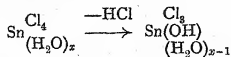
This process continues until stannic acid is produced, which must thus be regarded[2] as having the structure $[Sn(OH)_6]H_2$. The intermediate product, $SnCl_3(OH)$, can be isolated from the original solution by extraction with ether.

Complex Formation. — *Addition Products.* — These halides form addition products with neutral substances very readily. Thus stannic chloride gives such products with NO, NOCl, NH_3, H_2S, SCl_4, $SeOCl_2$, PH_3, PCl_5, $POCl_3$, N_4S_4, alcohol, ether and many other organic substances, the maximum co-ordination number 6 being usually attained. Titanic chloride forms addition products with all these and also with HCN, CNCl, CNBr; further, it forms compounds with alcohols, ethers, esters, ketones, alkyl cyanides, with organic nitrogen compounds, and also with those which contain sulphur (mercaptans, sulphides), and with acids, acid chlorides, etc. Platinic chloride, iridium tetrachloride and thorium chloride[3] also possess the property of forming addition products and probably other chlorides do the same. The compounds with ammonia are discussed on p. 332.

Hydrates and Basic Salts. — The tendency to form addition compounds is so great that in spite of the strong hydrolysis of these halides stable hydrates are formed. It is probable that the solid complexes containing water are less susceptible to hydrolysis than the uncombined salt. The following hydrates are typical :

$TiF_4 . 2H_2O$	$GeF_4 . 3H_2O$	$ZrF_4 . 3H_2O$
$ThCl_4 . 8H_2O$	$ThBr_4 . 8$, 10 and $12H_2O$	$ThI_4 . 10H_2O$
$SnCl_4 . 3, 4, 5$ and $8H_2O$	$SnBr_4 . 4H_2O$	
$PtCl_4 . 1, 4, 5, 7$ and $8H_2O$		
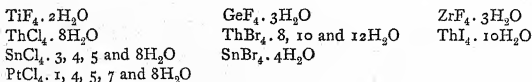
The hydrates of tin tetrachloride have been systematically examined by Meyerhoffer,[4] who found that the four hydrates reach their limits of stability at 83°, 63°, 56° and 19° respectively, and then break down into saturated solution and the next lower hydrate. The hydrates of the Pt halides are particularly interesting owing to the formation of complex aquo-acids. According to Hittorf and Salkowski[5] and

[1] *Ber.*, 1905, **38**, 2466.
[2] Bellucci and Parravano, *Z. anorg. Chem.*, 1905, **45**, 142.
[3] Rosenheim, *Z. anorg. Chem.*, 1903, **35**, 424 ; *Ber.*, 1904, **37**, 3662.
[4] *Bull. Soc. chim.*, 1891 [3], **6**, 85.
[5] *Z. physikal. Chem.*, 1899, **28**, 554.

Miolati,[1] $PtCl_4$ combines with water, like an anhydride, giving the compound $[PtCl_4(OH)_2]H_2$, which is one of the members of the series of hydroxochloroplatinic acids considered on p. 280. If the hydrolysis is increased, e.g. by the addition of ammonia, two chlorine atoms are removed and the tetrahydroxo-compound $[Pt(Cl)_2(OH)_4]H_2$ is formed. The replacement of three Cl atoms occurs in the interesting reaction of $Ba(OH)_2$ and H_2PtCl_6 in sunlight, giving $[PtCl(OH)_5]H_2$, and the complete elimination of Cl occurs when H_2PtCl_6 is boiled with sodium hydroxide and $[Pt(OH)_6]H_2$ is produced. The middle member of the series is unknown, but the pentachlor-compound is formed when the hexahydrate of chloroplatinic acid is carefully heated, this substance being hydrolysed by its own water of crystallisation:

$$[PtCl_6]H_2, \ 6H_2O \longrightarrow [PtCl_5(OH)]H_2 + HCl + 5H_2O.$$

In other salts the Cl is replaced by oxygen instead of by the hydroxyl group, giving oxy-halides. The oxygen occupies two co-valency positions, and the compounds formed have the general formula $M^{IV}OX_2$, where X represents the halogen present; these compounds can be made by dissolving the oxide or hydroxide of the metal in a solution of the halogen acid and evaporating the liquid. They are definite crystalline compounds.

The Zr compounds, $ZrOCl_2$, $ZrOBr_2$, $ZrOI_2$ crystallise in needles with $8H_2O$ and are easily soluble in water, from which solution they are precipitated on addition of the concentrated halogen acid. UOF_2 corresponds to the normal fluoride in colour and insolubility. The vanadium oxyhalides are also known ; $VOBr_3$ gives the yellow-brown deliquescent powder $VOBr_2$ on heating, and the grass green $VOCl_2$ gives a double compound with $PtCl_4$. The oxyfluoride VOF_3 is not known, but a blue di- and a green tetra-pyridinium chloride double salt have been prepared ; there are also blue double compounds of VOF_3 with halides of both alkali and heavy metals.

Double Halides.—The double halides of this group are numerous and stable. They are derived for the most part from the complex acids $[MX_6]H_2$, though the fluorides of thorium and uranium correspond to the acid $H[MF_5]$, and those of Zr, Pb and Sn to the acid $H_4[MF_8]$. The zirconium compound Na_5ZrF_9 is interesting, as the co-ordination number 8 is exceeded; but these few compounds are negligible in view of the overwhelming number of double halides which are salts of H_2MX_6. The central metal can be any of those in this group, and the only difficulty in preparing them arises from the tendency of the free halides to hydrolyse in aqueous solution. This occurs, for example, with tin iodide and zirconium chloride, but, using alcoholic solutions, the bluish-black salts of H_2SnI_6 and H_2ZrCl_6 with organic bases can be obtained. When the acids H_2MX_6 can be prepared in the free state they are much more proof against hydrolysis than the simple halides. The quadrivalent metal halides can often be isolated as

[1] *Z. anorg. Chem.,* 1900, 22, 463.

complex ions $[MCl_6]''$ when the halides themselves are unstable (cf. p. 324), as, for example, those of lead, manganese and antimony.

The tetrafluoride, bromide and iodide of lead are unstable as simple compounds, but the double salts are very stable and will bear heating to above 100° without decomposition. They are made by adding quadrivalent lead compounds (e.g. tetracetate, red lead) to solutions of the halogen acids containing the salt of a cation of large volume (K, NH_4, or, better, Rb or Cs, or organic cations like pyridinium or quinolinium).[1] The acid potassium salt, $K_3H[PbF_8]$, is worthy of note. The chlorosalts can also be prepared synthetically by passing chlorine through a suspension of lead dichloride in hydrochloric acid containing alkali chloride in solution. They are lemon yellow like the fluorides, the bromides are vermilion, the iodides brownish black or grey green.

Manganese gives yellow double fluorides when manganate solutions are treated with hydrofluoric acid[2]; free manganic acid is first formed (H_2MnO_4), which is then oxidised in part to permanganic acid and partly reduced to the MnF_4 state, with subsequent formation of M_2MnF_6. The preparation of the double chlorides, M_2MnCl_6, is less simple; but the calcium salt is formed when calcium permanganate is treated with concentrated hydrochloric acid and potassium chloride,[3] or when a solution of permanganate in glacial acetic acid is treated with hydrogen chloride gas. Chloromanganic acid is not very stable, and $MnCl_4$, $MnCl_3$ and free chlorine are found in equilibrium with it, and the complex acid of tervalent manganese is also formed. That an equilibrium exists is shown by the behaviour of manganese in electrolytic oxidation, when there are no definite steps in the series $Mn'' \longrightarrow Mn''' \longrightarrow Mn''''$; Mn''' is not represented as a definite stage, but is part of a continuous rise to the quadrivalent state. Double bromides and iodides of quadrivalent manganese are unknown, though $K_4Mn(CN)_8$ has been prepared.

The halogen compounds of quadrivalent antimony are still less stable. The violet-black double chloride and bromide are formed[4] when alkali chlorides are added to a hydrochloric acid solution containing equimolecular quantities of ter- and quinque-valent antimony. The slightly coloured solution contains only small quantities of H_2SbCl_6, but the double halide separates out owing to its low solubility, thus disturbing the equilibrium $2SbCl_4 \rightleftharpoons SbCl_3 + SbCl_5$. A rise in temperature favours the formation of $[SbCl_6]''$ complexes, and the reaction is not rapidly reversed on cooling, so that crystals of the double salts can be got by chilling the hot liquid, whereas they would not separate out but revert to the ter- and quinque-valent condition if

[1] See Brauner, Z. anorg. Chem., 1894, 7, 1, 18.
[2] Weinland and Lauenstein, Z. anorg. Chem., 1899, 20, 40.
[3] Weinland and Dinkelacker, Z. anorg. Chem., 1908, 60, 173.
[4] Weinland and Schmid, Ber., 1905, 38, 1080.

the solution were cooled slowly. Salts of this complex containing cations of small volume decompose even in the solid state, and thus become coloured after a time; they are metastable, and their period of existence is increased with the rapidity of the cooling of the liquid.

Metastable compounds of this type can be made more stable by being produced in admixture with isomorphous stable salts. Now all salts of the general formula $M_2^I M^{IV} X_6$, when M^I is K, NH_4, Rb, Cs are isomorphous, crystallising in the regular system, usually in octahedra; when, therefore, the labile compound, M_2SbX_6, is crystallised with the more stable compounds of lead, tin or platinum, M_2PbX_6, M_2SnX_6, M_2PtX_6, black crystals of the antimony compound are obtained and remain stable. Two molecules of $SbCl_4$ are necessary for the decomposition, $2SbCl_4 \rightleftharpoons SbCl_3 + SbCl_5$, and if one of the two is embedded in a crystal and separated from the other, the decomposition is inhibited.

Of the quadrivalent cerium halides, $CeCl_4$ has not been isolated; but if a ceric salt is dissolved in concentrated hydrochloric acid a deep red liquid is produced, which probably contains the acid H_2CeCl_6. It decomposes rapidly with evolution of chlorine, but if organic bases are added, their salts with this acid are obtained as yellow crystalline precipitates.[1]

The stability of these complexes, in which the anion is complex, depends very largely on the size of the cation attached to them, so that the free acid is often more difficult to isolate than the salts of alkali metals or of organic bases with it. The free acids have, however, been obtained in many instances, a process which is simpler when they crystallise with water of crystallisation. They are mostly stable in solution unless easily reduced like the lead and manganese compounds; the free acids of tin and platinum have been most thoroughly studied. Chlorostannic acid, $H_2SnCl_6 . 6H_2O$, is formed by the action of hydrochloric acid gas on the hydrate of stannic chloride. It is a white solid melting at 19°, and is very hygroscopic; the ammonium salt (pink salt) is the commonest salt, and it is employed in technical processes in preference to the simple chloride, as it is less hydrolysed in solution. Bromostannic acid contains more water of crystallisation and is amber coloured; iodostannic acid is deep blue-black in colour. This deepening of colour, which corresponds to that in the metal halides themselves, is very common in the complex halogen acids, the following being a good example:

H_2TiF_6	H_2TiCl_6	H_2TiBr_6	H_2TiI_6
Colourless.	Deep yellow.	Blood red.	Dark red.

The best known of the whole series is hexachloroplatinic acid, $H_2PtCl_6 . 6H_2O$, which forms brownish-red hygroscopic prisms. It is

[1] Koppel, Z. anorg. Chem., 1899, 18, 305.

produced when the metal is dissolved in *aqua regia*, or when the ammonia in the ammonium salt is removed with chlorine. The general behaviour of this acid has been previously mentioned on p. 329. It is a valuable reagent in analysis, for it gives yellow precipitates with cations of large volume, which are the more insoluble the greater the volume of the cation. They are all anhydrous octahedra, like the rest of the compounds of formula $M_2^IM^{IV}X_6$; the salts of cations of small volume crystallise only when laden with water of crystallisation—some have a remarkably large water content. It is greater still in the salts of the analogous bromo-acid H_2PtBr_6, and in the iodo-acid H_2PtI_6, which give carmine red and reddish-black tables respectively. The alkali salts of these acids are even more insoluble than those of the chloro-acids. The other metals of the platinum group give similar compounds, which cannot be discussed here for want of space; they have been studied in detail by Gutbier and his students, who have prepared many compounds of organic bases with these acids.

Few cyanides and thiocyanates of quadrivalent metals exist, for they cannot be made in the dry way, and they are hydrolysed to a high degree in aqueous solution. Even double cyanides are known only in isolated cases, but more double thiocyanates exist, *e.g.* those of platinum. The double cyanides of molybdenum and tungsten are yellow, and have the composition $M_4Mo(CN)_8$ and $M_4W(CN)_8$; their behaviour on oxidation, with permanganate for instance, is worthy of note.[1] They can be oxidised only to the quinquevalent state, *e.g.* to $M_3[Mo(CN)_8]$ although as a rule molybdenum and tungsten pass to the sexavalent condition on such treatment. It is not easy to explain this anomaly, but the complex is so stable that the free acid can be prepared. As has been previously mentioned, fluorides with the ion $[MF_8]$ also show abnormal behaviour, and it is probable that the close packing of the attached groups prevents the free operation of the maximum primary valency.

Ammines.—The halides of the quadrivalent metals form additive compounds with ammonia in great abundance. The usual co-ordination number is 8 for the halides of titanium, thorium chloride and tin iodide, which give octammines. But the capacity of these halides for addition of ammonia is by no means exhausted at this stage, and at temperatures below 0° larger quantities can be attached to the molecule. Thus both $ThCl_4$ and SnI_4 combine with 18 mols. of ammonia when cooled in an ordinary freezing mixture and $GeCl_4$ forms $GeCl_4$. $16NH_3$. It is possible that the substances thus formed are merely solid solutions of NH_3 in the ammine; liquid ammonia removes ammonium halide from the mass, so that "ammonolysis" is probably also one of the effects. This process is analogous to

[1] See Rosenheim and Dehn, *Ber.*, 1915, 48, 1167; Olsson, *Z. anorg. Chem.* 1914, 88, 49.

hydrolysis, the NH_2 group taking the place of the halogen atom in the same way that the OH group replaces the latter in hydrolysis, thus $MCl + 2NH_3 = M \cdot NH_2 + NH_4Cl$.

The Platinum Ammines and related Substances

The ammines of the platinum metals, and particularly of platinum itself, are the most extensive group of ammines formed by quadrivalent metals. As was noticed in cobalt and chromium in the tervalent class, the property of forming metal ammines to any extent is confined to a few metals, and this is true in the quadrivalent group as well. The platinum ammines can be taken as typical of the compounds as a whole. The co-ordination number is 6, and the types of ammines are in general those discussed previously (p. 310), though they are less variable in the acid radicals which occur in the complex. On the other hand, the neutral groups which can form part of the complex include some not met with in the cobalt- and chrom-ammines, *e.g.* compounds of sulphur, selenium and phosphorus. The platinum compounds can also exist in various stages of oxidation, and ammines of both bi- and quadri-valent platinum are common. The latter can therefore be made by a method not always available for the ammines of Co and Cr—the oxidation of the bivalent ammines, which, indeed, is one of the most useful means of preparation. The Co and Cr ammines are often made by oxidation processes (*e.g.* with atmospheric oxygen), but their bivalent ammines are very unstable and cannot easily be isolated.

The chief types of ammines of quadrivalent platinum are as follows:

$$[PtA_6]X_4 \quad [PtA_4Y_2]X_2 \quad [PtA_3Y_3]X \quad [PtA_2Y_4] \quad [PtAY_5]M \quad [PtY_6]M_2$$

(A = neutral group, Y = radical inside the complex, X = radical outside the complex, and M = a univalent metal.)
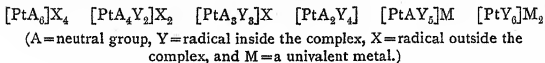
The type $[PtA_5Y]X_3$, though uncommon, has been prepared, *e.g.* $[Pt(NH_3)_5Cl]Cl_3$, obtained together with $[Pt(NH_3)_6]Cl_4$ by the action of liquid NH_3 on $(NH_4)_2PtCl_6$ in a sealed tube.[1] The formulation given above has been proved to be correct by conductivity measurements, which give the basicity of the complex. The complexes are so stable that the removal of co-ordinated groups is difficult, though halogen radicals can be extracted by prolonged digestion with silver salts.

The type $[PtA_6]X_4$.—Although many corresponding compounds $[MA_6]X_3$ have been made in the cobalt and chromium series, only a few of the platinum salts are known. The carbonate $[Pt(NH_3)_6](CO_3)_2$ is formed as a white powder when an ammoniacal solution of ammonium carbonate is electrolysed with platinum electrodes with alternating current below 0°. It is very stable when once formed, and gives several

[1] Tschugaev, *Compt. rend.*, 1915, 160, 840; 161, 699.

salts by double decomposition, and also a well-crystallised hydroxide, $[Pt(NH_3)_6](OH)_4$. They are also white and difficultly soluble in water, and like their analogues in the Co and Cr series give double compounds with chloroplatinic and chlorauric acids. So far no complexes of this type with neutral groups other than ammonia have been prepared.

The type $[PtA_4Y_2]X_2$.—These compounds can for the most part be prepared by the oxidation of the tetrammines of bivalent platinum, $[Pt(NH_3)_4]X_2$, using a source of the group it is desired to introduce as oxidising agent, when the compound of quadrivalent platinum is formed by simple addition, e.g.:

$$[Pt(NH_3)_4]^{\cdot\cdot} + 2NO_2 \longrightarrow [Pt(NH_3)_4(NO_2)_2]^{\cdot\cdot},$$
$$[Pt(NH_3)_4]^{\cdot\cdot} + Cl_2 \longrightarrow [Pt(NH_3)_4Cl_2]^{\cdot\cdot},$$
$$[Pt(NH_3)_4]^{\cdot\cdot} + H_2O_2 \longrightarrow [Pt(NH_3)_4(OH)_2]^{\cdot\cdot},$$
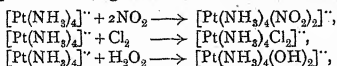
and similarly for the addition of Br_2, I_2, etc. They can also be obtained in some instances by treating other platinic compounds with concentrated acids, thus:

$$[Pt(NH_3)_4(OH)(NO_3)]^{\cdot\cdot} + H_2SO_4 \longrightarrow [Pt(NH_3)_4SO_4]^{\cdot\cdot} + HNO_3 + H_2O.$$
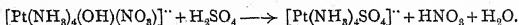
These salts are mostly white, but the NO_2-compound is sky-blue, the bromo-compound yellow, and the iodo-compound a dark brown. The acid radical outside the complex is the only one easily removed, but on boiling with water hydrolysis occurs, and compounds of the type $[Pt(NH_3)_4(OH)Y]^{\cdot\cdot}$ are formed. A few compounds are known in which organic bases take the place of the ammonia; if the acid radical is of basicity two or higher, the valency of the complex is lowered and univalent nuclei are formed, e.g.:

$$[Pt(NH_3)_4(PO_4)]X \quad \text{and} \quad [Pt(NH_3)_4(NO_2)(CO_3)]X.$$

The type $[PtA_3Y_3]X$.—Few compounds of this class are known; they are prepared in the same way as those of the preceding type. For instance, $[Pt^{IV}(NH_3)_3Cl_3]Cl$ is obtained when the platinous compound $[Pt^{II}(NH_3)_3NO_3]NO_3$ is boiled with *aqua regia*, as oxidation and replacement of the NO_3 groups by Cl occur simultaneously.

The type $[PtA_2Y_4]$.—These compounds exist in cis and trans forms:

Cis.   Trans.
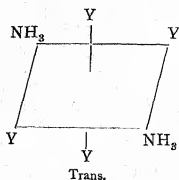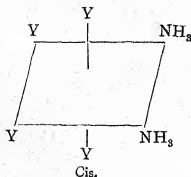
and like the compounds of the preceding type they are obtained by addition of the requisite acid radicals to the corresponding compounds of bivalent platinum, $e.g.$:

$$\text{trans}[Pt^{II}(NH_3)_2Cl_2] + Cl_2 \longrightarrow \text{trans}[Pt^{IV}(NH_3)_2Cl_4],$$
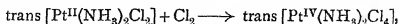
or by treating the platinic hydroxo-compound with acid:

$$[Pt(NH_3)_2(OH)_2(NO_3)_2] + 2HNO_3 \longrightarrow [Pt(NH_3)_2(NO_3)_4] + 2H_2O.$$
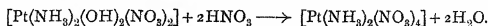
The acid radicals introduced need not be the same as those already present, $e.g.$ $[Pt(NH_3)_2(NO_2)_2] + Br_2 \longrightarrow [Pt(NH_3)_2(NO_2)_2Br_2]$, and as the complex can be hydrolysed, when compounds of this type are boiled with ammonia the hydroxo-compound $[Pt(NH_3)_2(OH)_4]$ is formed.

The trans compounds are mostly pale yellow, while the cis compounds are darker in colour.

There are a large number of compounds of this type in which the NH_3 is replaced by other neutral groups; they are made, like the ammines, by the oxidation of platinous complexes, or by boiling the chloroplatinates, when two molecules of acid are lost from the nucleus and can be replaced by bases originally outside the platinum complex, $e.g.$:

$$[PtCl_6](Hpy)_2 = [Pt(py)_2Cl_4] + 2HCl \qquad (py = pyridine).$$
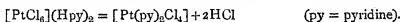
The following are a few examples of compounds of this type containing:

Collidine	$[Pt(C_8H_{11}N)_2Cl_4]$	Benzonitrile	$[Pt(C_6H_5 . CN)_2Cl_4]$
Dimethylpyrimidine	$[Pt(C_6H_8N_2)_2Cl_4]$	Methyl iso-oxazole	$[Pt(C_4H_5NO)_2Cl_4]$
Aminoacetic acid	$[Pt(NH_2CH_2CO_2H)_2Cl_4]$	Aminoacetic ester	$[Pt(NH_2 . CH_2CO_2C_2H_5)_2Cl_4]$
Pyrazole	$[Pt(C_3H_4N_2)_2Cl_4]$	Pyrazine	$[Pt(C_4H_4N_2)_2Cl_4]$
Triazole	$[Pt(C_2H_3N_3)_2Cl_4]$	Tetrazoline	$[Pt(CH_4N_4)_2Cl_4]$
Ethyl alcohol	$[Pt(C_2H_5OH)_2Cl_4]$	Alkyl or aryl sulphide	$[Pt(R_2S)Cl_4]$
Alkyl selenide	$[Pt(R_2Se)Cl_4]$	Ethyl phosphine	$[Pt(P(C_2H_5)_3)_2Cl_4]$
	$[Pt(PCl_5)_2Cl_4]$ $[Pt\{P(OC_2H_5)_3\}_2Cl_4]$		$[Pt\{OP(OC_2H_5)_3\}_2Cl_4]$, etc.

Of course, acid radicals other than Cl can enter the nucleus, but the chlorine compounds are the best known.

The type $[PtAY_5]M$.—These compounds contain a complex anion and are also made from the corresponding platinous compounds; they are intermediate products in the formation of the substances discussed in the last paragraph, and can thus be obtained from the chloroplatinates if the heating is only carried to the point at which one molecule of hydrochloric acid is liberated:

$$[PtCl_6](Hpy)_2 \longrightarrow [PtpyCl_5](Hpy) + HCl.$$
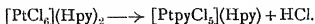
The pyridinium group which forms the cation can be replaced by metals.

Multinucleate Complexes of Platinum and Palladium.—Among the multinucleate compounds of these metals is one made from bis-trialkyl-phosphine palladous chloride; with ammonium pallado-chloride, $[Pd(R_3P)_2Cl_2, PdCl_2]$ is formed, which Mann and Purdie[1] have shown to exist in three varieties. They formulate these as follows:

$$
\text{I.} \quad
\begin{matrix}
R_3P \\ R_3P
\end{matrix}
\!\!\searrow\!\!\nearrow Pd
\begin{matrix}
Cl \\ Cl
\end{matrix}
Pd
\begin{matrix}
Cl \\ Cl
\end{matrix}
\qquad
\text{II.} \quad
\begin{matrix}
R_3P \\ Cl
\end{matrix}
Pd
\begin{matrix}
Cl \\ Cl
\end{matrix}
Pd
\begin{matrix}
PR_3 \\ Cl
\end{matrix}
$$

$$
\text{III.} \quad
\begin{matrix}
R_3P \\ Cl
\end{matrix}
Pd
\begin{matrix}
Cl \\ Cl
\end{matrix}
Pd
\begin{matrix}
Cl \\ PR_3
\end{matrix}
\qquad R = \text{alkyl group}
$$
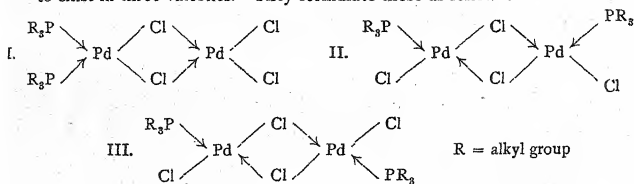
Some compounds assumed to contain tervalent Pt, of which the simplest types are $PtCl_3$ and $M^I Pt(CN)_4$, may be of the multinucleate type. For example, for the compound $PtCl_3(EtNH_2)_4 2H_2O$ Drew and Tress[2] use the formula:

$$
\left[(EtNH_2)_4 \overset{IV}{Pt} \!\! \begin{matrix} \\ | \\ Cl \end{matrix} \!\!\!—\!\!\! \begin{matrix} \\ | \\ Cl \end{matrix} \overset{IV}{Pt}(NH_2Et)_4 \right] Cl_4 . 4H_2O
$$
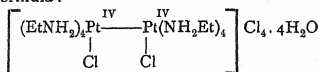
but Mann and Purdie prefer:

$$
\left[(EtNH_2)_4 \overset{IV}{Pt} \begin{matrix} Cl \\ \diagup \diagdown \\ Cl \end{matrix} \overset{II}{Pt}(NH_2Et)_4 \right] Cl_4 . 4H_2O
$$
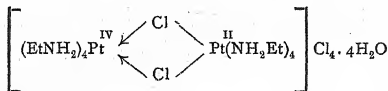
Similarly, $PtCl_3 . en$ is formulated:

$$
\left[en \Longrightarrow \overset{IV}{Pt} \begin{matrix} Cl\ Cl \\ \\ | \\ Cl \end{matrix} \begin{matrix} Cl\ Cl \\ \\ | \\ Cl \end{matrix} \overset{IV}{Pt} \Longleftarrow en \right] \quad \text{or}
$$

$$
\left[en \Longrightarrow \overset{II}{Pt} \begin{matrix} Cl\ Cl \\ \\ | \\ Cl \end{matrix} \begin{matrix} Cl \\ \diagup \diagdown \\ Cl \end{matrix} \overset{IV}{Pt} \begin{matrix} Cl \\ \\ | \\ Cl \end{matrix} \Longleftarrow en \right]
$$
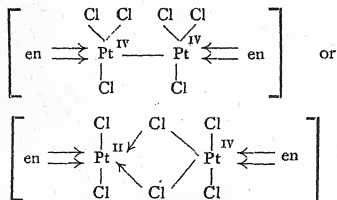
In Drew's formulation Pt is shown entirely as quadrivalent whereas Mann's formulae contain both bi- and quadri-valent Pt, each type having a co-ordination number of 6.

[1] *J. Chem. Soc.*, 1936, 873.   [2] *J. Chem. Soc.*, 1935, 1244.

By the action of aqueous ammonia on $[PtI_2(NH_3)_4]X_2$ Cleve obtained, by loss of $2HX$ per molecule:

$$\left[\begin{array}{c} NH_3 \\ NH_3 \rightarrow Pt \\ NH_3 \\ Y \end{array} \begin{array}{c} NH \\ NH \end{array} \begin{array}{c} NH_3 \\ Pt \leftarrow NH_3 \\ NH_3 \\ Y \end{array}\right] X_2$$
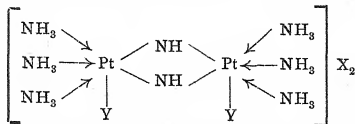
and by treatment with nitric, hydrochloric or sulphuric acids, other binucleate ammines of the type:

$$\left[\begin{array}{c} NH_3 \\ NH_3 \rightarrow Pt \\ NH_3 \\ Y \end{array} \begin{array}{c} NH_2 \\ NH_2 \end{array} \begin{array}{c} NH_3 \\ Pt \leftarrow NH_3 \\ NH_3 \\ Y \end{array}\right] X_4$$

are formed, where $X = NO_3$, Cl or $\frac{1}{2}SO_4$
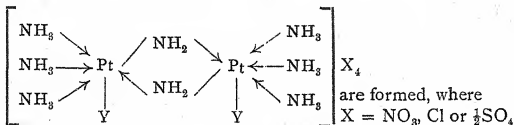
The Complex Compounds of Bivalent Platinum

Platinum shows a co-ordination number 4 when in the bivalent state, and the following types of compounds are known (abbreviations as on p. 333):

$$[Pt(NH_3)_4]X_2 \qquad [Pt(NH_3)_3Y]X \qquad [Pt(NH_3)_2Y_2]$$
$$[Pt(NH_3)_2Y_2]M \qquad\qquad [PtY_4]M_2.$$
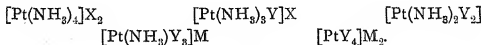
The compounds $[Pt(NH_3)_4]X_2$.—The chloride $[Pt(NH_3)_4]Cl_2$, H_2O, Reiset's salt, is the usual raw material for the preparation of the compounds of this type. It is made synthetically by the action of excess of aqueous ammonia on platinous chloride, and forms white crystals, which by suitable double decomposition give the well-known salts of the complex with other acids. The free base, $[Pt(NH_3)_4](OH)_2$, is also stable. The green salt of Magnus, $[Pt(NH_3)_4]PtCl_4$, is the salt of the complex with chloroplatinous acid, and is incidentally a polymer of Peyrone's salt, $[Pt(NH_3)_2Cl_2]$, which exists in cis and trans forms, as can be predicted from the co-ordination theory. A third variety has more recently been obtained.[1] All three forms were considered to be monomeric although the evidence does not appear to be entirely conclusive, and they were represented as structural isomerides without reference to stereochemical considerations, viz.:

$$\begin{array}{cc} Cl & NH_3 \\ & Pt \\ NH_3 & Cl \end{array} \qquad \begin{array}{cc} Cl.NH_3 & \\ & Pt \\ NH_3 & Cl \end{array} \qquad \begin{array}{cc} Cl.NH_3 & \\ & Pt \\ Cl.NH_3 & \end{array}$$
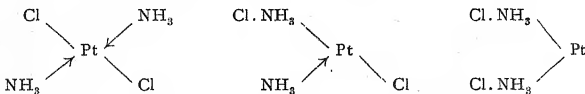
[1] Drew, Pinkard, Wardlaw and Cox, *J. Chem. Soc.*, 1932, 988.

These views followed largely from a study of $PtCl_2 . 2Et_2S$ which was shown to exist in two forms, best represented as :
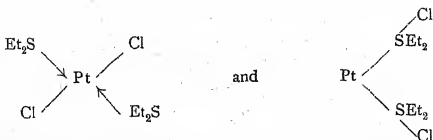
the chlorine being ionised in the second compound.[1] Magnus's green salt is formed by treating $PtCl_2$ or H_2PtCl_4 with ammonia, when the insoluble salt separates—another example of the low solubility of salts of a complex of large volume with a voluminous anion (*cf.* p. 301) ; with excess of ammonia, Reiset's salt is formed.

The ammonia in these compounds can be replaced by many other neutral groups, *e.g.* hydrazine, hydroxylamine, nitrogenous organic bases, carbylamine (RNC), thiourea $(CS(NH_2)_2)$ and their substitution products sulphines (SR_2), selenines (SeR_2), phosphines (PR_3), arsines (AsR_3), etc. The substitution is easily effected up to the stage $[PtA_2Y_2]$, as, for example, when a solution of platinous chloride is dropped into excess of thiourea dissolved in water, but prolonged boiling is necessary to remove the acid radical from the complex.   Compounds with various neutral groups can also be obtained (*e.g.* $[Pt(NH_3)_2(NH_2OH)_2]Cl_2$, usually by mere addition of fresh neutral groups to a complex containing two groups, $[Pt(NH_3)_2Cl_2]$. These compounds show the same isomerism as those from which they are made, and they have been prepared with carbon monoxide, acid esters (*e.g.* $P(OCH_3)_3$) and amides (*e.g.* $P(NH_2)_3$) as the second neutral groups.

The compounds $[Pt(NH_3)_3Y]X$.—Among the rare examples of this type are $[Pt(NH_3)_3Cl]Cl$, formed with other products when $[Pt(NH_3)_4]Cl_2$ is heated with hydrochloric acid, or by the action of a little ammonia on $[Pt(NH_3)_2Cl_2]$; sulphines are formed by an analogous reaction : $[Pt\{(CH_3)_2S\}_2Cl_2] + (CH_3)_2S \longrightarrow [Pt\{(CH_3)_2S\}_3Cl]Cl$. These compounds are all white and the method of introducing different neutral groups into the complex is indicated by the manner of preparation.

The compounds $[PtA_2Y_2]$.—The substances in this group—the largest class of complex compounds of bivalent platinum—occur in cis and trans forms, thus :
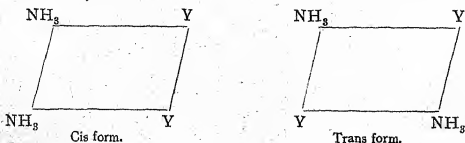
[1] Angell, Drew and Wardlaw, *J. Chem. Soc.*, 1930, 349 ; Drew and Wyatt, *ibid.*, 1934, 56.

They are mostly pale yellow in colour and can be made from the chloride. Thus cis $[Pt(NH_3)_2Cl_2]$ is made by adding ammonia to $PtCl_2$ or K_2PtCl_4. The trans compound is left when $[Pt(NH_3)_4]Cl_2$ is heated, and conversely both cis and trans compounds take up ammonia and other neutral groups to form tetrammines and substances of analogous composition. Further, by addition of Cl, Br, NO_2, etc., compounds of quadrivalent platinum are formed (see p. 333). The chlorine atoms within the complex are not very firmly bound and undergo double decomposition without much difficulty. Thus $[Pt(NH_3)_2(NO_3)_2]$ can be made by treating the chlorine compound with silver nitrate, while silver sulphate gives $[Pt(NH_3)_2SO_4]$, though both these reactions are noticeably slower than the usual ionic reactions with silver salts.

The conductivity of these compounds in aqueous solution is practically nil just after a solution is made, but gradually increases owing to hydrolysis of the complex. Thus a dilute solution of the cis-chloride gave the following results:

Time   2   4   10   15   30   180   mins.
μ 1·81   2·41   2·61   4·33   11·03   21·87 reciprocal ohms.

The replacement of the chlorine in the complex can be effected by reactions which do not involve the precipitation of one of the products; thus oxalic acid gives $[Pt(NH_3)_2C_2O_4]$, potassium cyanide gives $[Pt(NH_3)_2(CN)_2]$, etc. The derivatives with radicals of organic acids containing sulphur are particularly numerous. The ammonia in the complex can naturally be replaced by other neutral groups and the most varied amine, carbonyl, sulphur, selenium, phosphorus, arsenic and antimony derivatives can be obtained by the usual methods. The carbonyl compound $[Pt(CO)_2Cl_2]$ can be made in the dry way by passing carbon monoxide over platinous chloride. The internally complex compounds (cf. p. 340) of this group may also be mentioned, in which aminoacetic acid, dioximes, and especially radicals containing sulphur occupy the co-ordination positions.[1]

CO$_2$ O$_2$C   RC=N→O   HON=CR   HO$_2$C . CH$_2$. S . CH$_2$. CO$_2$

CH$_2$ Pt CH$_2$ Pt   Pt

NH$_2$ NH$_2$ RC=NOH   O←N=CR   HO$_2$C . CH$_2$. S . CH$_2$. CO$_2$
Aminoacetate.   Di-R-dioxime.   Thio-di-glycollate.
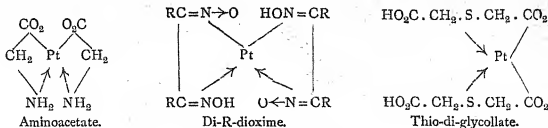
The compounds $M[PtAY_3]$.—The potassium salt is formed by the action of a limited quantity of ammonia on $[PtCl_4]K_2$, when a chlorine atom is removed from the complex; the ammonium salt is made by introducing a chlorine atom into the complex $[Pt(NH_3)_2Cl_2]$ by boiling it with hydrochloric acid. These salts are orange yellow in colour, and the complex is so strong that sodium hydroxide fails to displace the ammonia from it, and the usual variety of compounds can be produced by replacing the ammonia by other groups. Those which contain CO are of especial interest, e.g. $[Pt(CO)Cl_3]M$, and those

[1] Ramberg, Z. anorg. Chem., 1906, 50, 443.

which have ethylene hydrocarbons in place of the ammonia, *e.g.* Zeise's salt,[1] $K[PtCl_3(C_2H_4)]Cl . H_2O$, which is formed when potassium chloride is added to a solution of platinous chloride saturated with ethylene, or when a solution of $PtCl_4$ in alcohol is evaporated and then precipitated with potassium chloride, the alcohol being dehydrated in the process. Higher alcohols behave in a similar manner.

The compounds $M_2[PtY_4]$.—Free chloroplatinous acid, H_2PtCl_4, is formed when platinous chloride is dissolved in hydrochloric acid, or can be obtained by reduction of chloroplatinic acid, H_2PtCl_6, by mere heating or by the action of reducing agents. The purple-red solution is stable in the presence of excess of HCl, but otherwise hydrolysis sets in and $[Pt(OH)Cl_3]H_2$ or $[PtOCl_2]H_2$ is formed, which by auto-oxidation and reduction gives free platinum and H_2PtCl_6. The salts are easily soluble in water, in contrast to the chloroplatinates, of which even the alkali salts are not soluble. They are red and can be made by reducing the chloroplatinates in the dry way. The corresponding bromine compounds are almost black, and have similar properties, but the iodine complexes are not known. The cyanogen compounds $M_2[Pt(CN)_4]$ form beautiful crystals which are fluorescent and pleochroic to an extent observed in very few substances. The colour varies from pale yellow to deep blue, or from sea green to brownish red, according to the direction of observation. The colour also varies with the age of the preparation, and these substances are almost colourless when first made. The phosphorescence shown by these salts when exposed to certain radiations has led to their use as screens for X-ray work, the barium salt being widely employed. The compounds can be prepared by the action of cyanides on a solution of platinous chloride; the potassium salt is formed when metallic platinum is boiled with potassium cyanide, owing to the oxidising action of the air; or if platinic complexes are treated with KCN the platinous cyanides are formed, as those of quadrivalent platinum are not stable; the platinous ammines are very stable—much more so than those of Ni and Pd. The alkali and alkaline earth salts are soluble, but those of the heavy metals, especially that of copper, are only slightly soluble.

Complex thiocyanates are also known ; they are red and soluble in water. The complex compounds of the other platinum metals have been studied by Gutbier, but no more than a mention of them is possible in this volume.

Internally Complex Compounds

Compounds are described as internally complex when they do not give rise to ions in solution. Examples of this class are the heavy metal salts of aminoacetic acid, *e.g.* the copper salt

[1] *Pogg. Ann.*, 1831, **21**, 517.
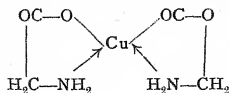
Copper has here the co-ordination number 4, two of the positions are taken up by the NH_2 groups and the chains attached to them, in the same way that these positions can be occupied by ammonia, while the other two places are occupied by the oxygen of the carboxyl group and the residue attached to it. The compound is a true copper salt, inasmuch as the metal is attached by primary valencies, and the ring formation is caused by the NH_2 groups being also joined to the Cu atom. The possibility of formation of this type of structure is determined, as in analogous cases in organic chemistry, by the number of groups in the chains. Chelation takes place most readily with five or six groups in the chain, owing to steric conditions such as are summarised in Baeyer's Strain Theory.

As the carboxyl group in this system occupies one of the co-ordination positions, it can be predicted that no copper ions will appear in solution, for the same reasons that the compound $[Co(NH_3)_3Cl_3]$ gives no cobalt ions, and it is found in practice that the aqueous solution of copper aminoacetate is almost non-conducting. The substance is, in fact, no more a salt than the cobalt compound. As, however, the stability of the complexes of this kind is variable, some of them conduct the electric current in solution. Thus in the silver ammonia complex $[Ag(NH_3)_2]^{\cdot}$, enough decomposition occurs in solution to give some silver ions, and some of the salts of aminoacetic acid of general formula $(NH_2CH_2.COO)_2M$ are ionised in the normal way in solution. The formation of these internal complexes depends on the metal atom, the property of co-ordinating NH_2 groups or ammonia being specific and most potent in copper, nickel, palladium and platinum. The corresponding salts of the alkali metals are all ionised normally and show high conductivity, for the alkali metals show but little tendency to form complexes with ammonia.

Some very interesting co-ordination compounds of the alkali metals have, however, been obtained.[1] The sodium salt of o-nitrophenol yields an additive compound with salicylaldehyde formulated as :
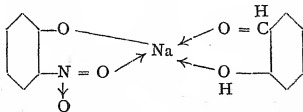
[1] Sidgwick and Plant, *J. Chem. Soc.*, 1925, **127**, 209 ; Sidgwick and Brewer, *ibid.*, 2379 ; King and Rutherford, *ibid.*, 1931, 3131 ; Brady and Bodger, *ibid.*, 1932, 952 ; Brady and Porter, *ibid.*, 1933, 840.

Lithium salicylaldehyde dihydrate:

$$
\begin{array}{c}
\text{H} \\
\text{—C = O} \diagdown \qquad \diagup \text{OH}_2 \\
\qquad\qquad \text{Li} \\
\text{—O} \diagup \qquad \diagdown \text{OH}_2
\end{array}
$$
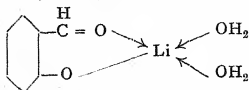
is likewise co-ordinated, for, although it is a dihydrate, it is soluble in toluene. Similarly, sodium benzoylacetone dihydrate dissolves in organic

$$
\begin{array}{c}
\overset{-}{\text{C}_6\text{H}_5\text{—C—O}}\ \overset{+}{\text{Na}} \\
\diagdown\diagdown \\
\text{CH} \\
\diagdown \\
\text{CH}_3\text{—C = O}
\end{array}
$$

solvents but the anhydrous salt is a polar compound.
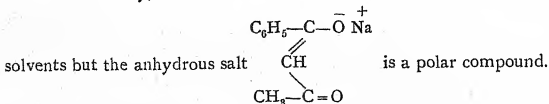
All the alkali metals form co-ordination compounds

$$
\begin{array}{c}
\qquad\qquad\qquad \text{H} \\
\text{—O} \diagdown \qquad \diagup \text{O} \\
\qquad\qquad \text{M} \\
\text{—C = O} \diagup \qquad \diagdown \text{O = C—} \\
\text{H} \qquad\qquad\qquad \text{H}
\end{array}
$$
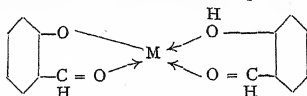
with salicylaldehyde and in the Rb and Cs compounds a further molecule of the aldehyde will co-ordinate giving a co-ordination number of 6.

When the complex is so stable that no metal ions are present in solution the compound fails to give the ordinary reactions of the metal. It is also not to be expected that the internally complex compounds will have the same colour as the ordinary salts of the metal, as even hydrates differ in colour from the anhydrous salts. The solubility of these complex salts is often markedly low; for the solubility of salts can often be attributed to the co-ordination of solvent molecules, whereby the solute becomes more similar to the solvent, and when the co-ordination positions are already occupied this factor in the promotion of solubility becomes inoperative. The capacity of various neutral groups to form internal complexes with certain metals is a useful weapon in analytical separations and is widely used.

It is mostly organic radicals which form these internally complex compounds, as they comprise chains of sufficient length to give five- or six-membered rings; examples of purely inorganic chelate compounds of Co and Rh are given on p. 297 and of certain multinucleate ammines on pp. 321 and 322. The following conditions are essential for the formation of the rings: 1. The radical must contain an acidic group such as OH- or NH-, which can take up one of the primary valencies of the metal in salt formation. 2. Groups must be present which can become co-ordinated with the central atom through their lone pair of electrons, e.g. through O as in water, through N as in ammonia, etc. 3. Further, these last radicals must be separated from the replaceable H atom by chains of suitable length for the production of five- or six-membered rings.

These conditions are fulfilled by the α- and β-amino-acids, the α-hydroxyacids, $R . CH(OH)COOH$, and the corresponding β-acids.

Thus ferric tartrates have been formulated[1] as:

$$\left[H_2O \longrightarrow Fe \begin{array}{c} O-C=O \\ | \\ O-CH \\ | \\ O-C.H.\overset{-}{C}O_2 \end{array} \right] \overset{+}{N}a \qquad \text{and}$$

$$\left[Fe \left(\begin{array}{c} O-CH-\overset{-}{C}O_2 \\ | \\ O-CH-\overset{-}{C}O_2 \\ H \end{array} \right)_3 \right] \overset{+}{N}a_6$$
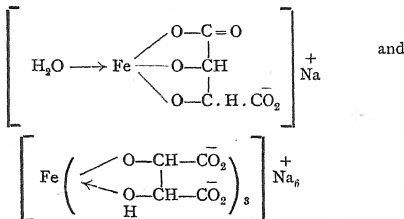
Tartar emetic is represented[2] as:

$$\left[H_2O \longrightarrow Sb \begin{array}{c} O-C=O \\ | \\ O-CH \\ | \\ O-CH-\overset{-}{C}O_2 \end{array} \right] \overset{+}{K}$$
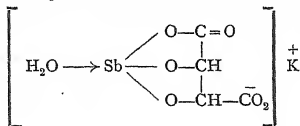
Malic and tartaric acids are common in these complexes, and copper tartrate is a typical internally complex salt*:

$$\begin{array}{cccc} O-cu\leftarrow OH & HO\rightarrow cu-O \\ | & | & | & | \\ CO-CH-HC-CO. \end{array}$$
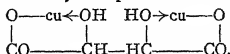
The copper is therefore not precipitated by reagents which would give precipitates of too high a solubility product, but on treatment with H_2S the complex is broken up, as the concentration of copper ions exceeds the solubility product of the sulphide. It is well known that the presence of tartrates inhibits many of the reactions of tervalent iron, aluminium and chromium, and it is probable that this is also due to the formation of internally complex compounds.

Acetylacetone, $CH_3 . CO . CH_2 . CO . CH_3$, gives complexes of this type of great theoretical interest. The enol form has a H atom replaceable by metals (using a covalency), and in the 1.6 position to it is an O atom which can be linked by its lone pair of electrons, thus:

$$\begin{array}{c} \overset{5}{C}H_3-\overset{4}{C}-\overset{}{C}H=\overset{3}{C}-CH_3 \\ \| \quad\quad | \\ \underset{6}{O} \quad \underset{1}{H}-\underset{2}{O} \end{array} \qquad\qquad \begin{array}{c} CH_3-C-CH=C-CH_3 \\ \| \quad\quad\quad | \\ O \rightarrow M-O \end{array}$$

[1] Franke, *Annalen*, 1931, **486**, 242 ; Pariselle and Delsal, *Compt. rend.*, 1934, **198**, 83.
[2] Reihlen and Hezel, *Annalen*, 1931, **487**, 213.
* Symbols printed with a small initial letter indicate equivalents of the element : thus $2cu = Cu$; $3al = Al$.

and complex acetylacetonates of many elements can therefore be obtained. The following are examples of such complexes, acetylacetone being represented by ac:

$[M(ac)_3]$, where $M = Al$, Ga, In, Sc, Y, Ce^{III}, V^{III}, Mn^{III}, Co^{III}.

$[M(ac)_4]$, where $M = Zr$, Hf, Ce^{IV}, Th, U^{IV}.

Quadrivalent vanadium forms $[O:V(ac)_2]$ and sexavalent molybdenum and uranium give $[MoO_2(ac)_2]$ and $[UO_2(ac)_2]$, presumably

$$\begin{array}{ccc}
& & O \\
\diagup C(CH_3) - O \diagdown & \| & \diagup O = C(CH_3) \\
CH & U & CH \\
\diagdown C(CH_3) = O \diagup & \nearrow \| & \diagdown O - C(CH_3) \\
& O &
\end{array}$$

A number of complexes obtained with this grouping cannot be regarded as internally complex, within the terms of the definition; such substances are, for example,

$$[B(ac)_2]Cl, \quad [M(ac)_3]Cl, \text{ where } M = Si, Ge, Ti, Zr.$$

These compounds are often stabilised by formation of their ferrichlorides $[M(ac)_3]FeCl_4$, aurichlorides $[M(ac_3)]AuCl_4$, etc. Germanium and tin also form $[M(ac)_2Cl_2]$ and the compound of univalent thallium is $[Tlac]$; quadrivalent titanium also gives $[Ti(ac)_2][TiCl_6]$, and the following is also interesting: $K[Pt^{II}(ac)Cl_2]$.

The acetylacetonates of the rare earths are particularly valuable, as they volatilise unchanged and are soluble in many organic solvents, and can thus be used for the determination of molecular weights, as well as for the separation of these elements from one another.

The internal complexes of the α-dioximes are also of importance. The formation occurs thus:

$$\begin{array}{cc}
HON:C.R & \\
| & \text{or} \\
HON:C.R &
\end{array}
\quad
\begin{array}{c}
O \\
\nwarrow \\
H - N = CR \\
| \\
HO - N = CR \\
\text{Oxime.}
\end{array}
\qquad
\begin{array}{cccc}
O & & & \\
\uparrow & & & \\
CH_3.C:N & & HON:C.CH_3 \\
| & \searrow Ni \swarrow & | \\
CH_3.C:NOH & & N:C.CH_3 \\
& & \downarrow \\
& & O \\
& \text{Nickel complex.} &
\end{array}$$

The nickel complex with dimethylglyoxime formulated above is one of the most useful of these complexes, as it is formed quantitatively as a red insoluble precipitate when the oxime is added to a solution of a nickel salt. It is thus of considerable analytical value, especially in the separation of nickel from cobalt. Dimethylglyoxime gives precipitates with metals of the eighth group, mostly insoluble and highly coloured (Fe^{III}, Co^{III}); the complexes with bivalent Pt and Pd volatilise unchanged at a high temperature *in vacuo* (Tschugaev). The stereochemistry of such compounds is dealt with on pp. 348-354. This

organic group can also enter into cobaltammines, and anhydrous cobaltous chloride in dry acetone solution gives red

$$\left[\left(\begin{array}{l} CH_3-C=N \\ CH_3-C=N \end{array}\right)_2 \overset{OH}{\underset{OH}{\Big\langle}} \rightarrow Co \right] Cl_2$$

which is easily converted by water[1] to green

$$\left(\begin{array}{l} CH_3-C=N \\ CH_3-C=N \end{array}\right)_2 \overset{OH}{\underset{OH}{\Big\langle}} \rightleftharpoons Co\overset{Cl}{\underset{Cl}{\Big\langle}}$$

Another compound of analytical[2] importance is the cobalt complex

with α-nitroso-β-naphthol, $N=O$ and $-OH$, which possibly reacts in the

quinonoid form $N-OH$ and $=O$ to give $\left(\begin{array}{l} N-O \\ =O \end{array}\right)_3 Co$.

Nitrosophenylhydroxylamine[3] gives insoluble precipitates with copper and iron, whence it is known as " Cupferron," and this provides a method of separating these metals from others whose complexes are either soluble under the conditions of precipitation or not formed at all.

Benzoinoxime gives with ammoniacal copper solutions containing tartrate a green precipitate of an unusual type $\begin{array}{l} C_6H_5-C=N-O \\ C_6H_5-C\ \ \ \ \ \ -O \end{array}\Big\rangle Cu$;
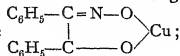
copper by this means can be separated from many other metals.[4]

Again, the complexes formed by 8-hydroxyquinoline ("oxine")

[1] Thilu and Heilbron, *Ber.*, 1931, 64[B], 1441.

[2] Mayr and Feigl, *Z. anal. Chem.*, 1932, 90, 15.

[3] Baudisch, *Chem. Zeit.*, 1909, 33, 1298.

[4] Feigl, *Ber.*, 1923, 56, 2083.

serve for a variety of separations and determinations of metals,[1] owing to their differing solubilities in media of different pH, in presence of different complex formers, etc. The complexes formed, as with acetylacetone are of varied types; for example:

where M is Zn, Cu, Cd, Mg, Ni, Co and MR_3, where M is Al, Bi, Fe^{III} ($R = C_9H_6ON$). The compounds of Ti^{IV}, Mo^{VI}, V^V, U^{VI} and Th^{IV} are $TiOR_2$, MoO_2R_2, $V_2O_3R_4$, UO_2R_2 . RH and ThR_4 . RH; one molecule of oxine is expelled by heating the complexes of U and Th.
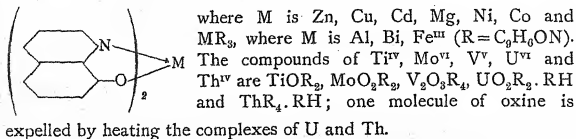
A number of materials used in spot tests in qualitative analysis probably form such internal complexes, but in many cases their constitution is by no means definitely established; for example, dithizone

$$C_6H_5—NH \cdot NH$$
$$C_6H_5—N:N$$

CS forms an intensely red compound with lead, which is soluble in chloroform, and rubeanic acid (dithiooxamide) gives an olive green complex with copper salts which may be
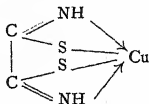
Co-ordination Compounds of Hydrogen

In some circumstances hydrogen can link together two electronegative elements. This tendency is shown in diminishing intensity by elements of the first short period, viz. F—H—F, O—H—O, N—H—N. In the second short period it appears only for Cl—H—Cl and then only feebly. At first it was assumed that this type of linkage resulted from covalently united hydrogen accepting two more electrons to form a shell of 4, presumably with 2 in the K and 2 in the L levels, e.g.

$$:\ddot{F}:H:\ddot{F}:H \qquad \text{or} \qquad F—H \leftarrow F—H$$
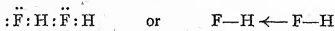
Such a shell is highly improbable, for it is contrary to Pauli's exclusion principle (see p. 4), and if formed, should be highly unstable. It is known, however, that elements often show their highest valency with fluorine, e.g. in IF_7, SF_6.

Since the hydrogen atom can form only one covalent bond, it follows that when it shows co-ordination number 2, the second bond must be due to ionic forces. Thus hydrogen bonds are formed only between atoms of the most electronegative elements as indicated

[1] See Berg, "Das Oxychinolin," *Die Chemische Analyse*, Band 34, Stuttgart, 1935.

above. The HF_2^- ion must be regarded as resonating between the structures

$$(a)\ :\ddot{F}:\ H\quad F^-$$
$$(b)\ F^-\ H^+\ F^-$$
$$(c)\ F^-\ H\quad :\ddot{F}:$$
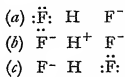
and similarly the $N-F-H$ bond is the resultant, so to speak, of the structures

$$(d)\ N:\ H\quad F^-\ \text{and}\ (e)\ N^-\ H^+\ F^-.$$
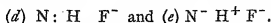
In these cases the attractive forces operate mainly in (b) and (e). In $O-H-O$ linkages it is found that the $O-H$ internuclear distance is not the same for both pairs of atoms, indicating again that one of the bonds is largely covalent, and the other largely ionic. This is shown by writing the formula $O-H\cdots O$.

The polymerisation of so many compounds containing hydroxyl groups may likewise be due to a similar cause, but representations, such as

$$\begin{array}{ccc} H & H & H \\ | & | & | \\ H-O & \cdots\ H-O & \cdots\ H-O \end{array} \text{ for water and } \begin{array}{ccc} R & R & R \\ | & | & | \\ H-O & \cdots\ H-O & \cdots\ H-O \end{array}$$
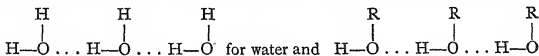
for alcohols suffer from the same defect. Compounds formed by ethers and alcohols might be similarly represented as $R_2O\ \cdots\ H-O-R$.

Co-ordinated hydrogen in the nitrogen series is met with in ammonium hydroxide, $H_3N\ \cdots\ H-OH$ and in the substituted types $RH_2N\ \cdots\ HOH$, $R_2HN\ \cdots\ H-OH$ and $R_3N\ \cdots\ H-OH$. Such compounds are weak bases, but the quaternary ammonium hydroxides are strong bases, indicating a difference in structure, thus $R_4\overset{+}{N}\overset{-}{O}H$ The infra-red absorption spectrum of ammonia shows that it, too, is slightly associated, $H_3N\ \cdots\ H-NH_2$, but all these co-ordinated formulae confer on hydrogen a shell of 4 electrons.

Valuable evidence concerning such structures was obtained[1] from a study of the boiling points and solubilities of certain o-, m- and p-substituted phenols, containing particularly the groupings $-NO_2$, $-CHO$ and $-Cl$. The o-compounds are markedly more volatile, less soluble in water, and more soluble in benzene than are the m- and p-forms, indicating that the o-varieties are internal complexes such as

 and
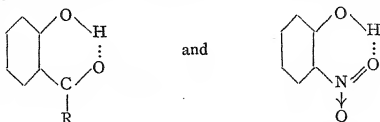
[1] Sidgwick and Callow, *J. Chem. Soc.*, 1924, **125**, 527; Sidgwick, *ibid.*, 2672. See also Sidgwick and Bayliss, *ibid.*, 1930, 2027.

whereas in the case of the *m*- and *p*-compounds, association such as
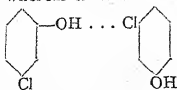
would still leave polar groups free. If, however,

the —OH group is converted into —OCH$_3$, the *o*-, *m*- and *p*-series of
ethers are very similar in properties, and behave as unassociated
non-polar substances.

The strain in such 6-membered rings containing co-ordinated
hydrogen, as represented above, would be small, and the difficulty in
these formulations is overcome by assuming that the substance is
actually a *resonance hybrid* or *mesomeride* of the two varieties, *e.g.*
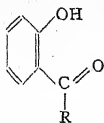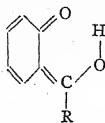
Such a mesomeric substance is a single variety intermediate between
the two formulations shown, and is more stable than either of them.
It is not necessarily halfway between the structures but will be situated
much nearer to the more stable variety. It cannot be represented by
any single formula by any of the usual methods, but for convenience
it may be regarded as involving single electron linkages between the
hydrogen and the attached groups. In this manner, the stable shell
of two electrons of combined hydrogen would be retained. The only
real justification which can be claimed for this singlet formula is that
it gives a concrete representation of a type intermediate between the
two extremes. The polymerisation in the other cases, namely, that of
hydrogen fluoride, of water, alcohols and ammonium hydroxides is
likewise explained by resonance.

Stereochemistry of Compounds of Co-ordination No. 4

The evidence of spatial distribution of groups attached to elements
of co-ordination number 6 is entirely in favour of an octahedral
configuration. In compounds of co-ordination number 4, however, the
evidence for some elements favours a tetrahedral distribution, for others,
a planar arrangement; the valency direction for a particular element
may be either tetrahedral or planar according to the nature of the
attached groups.

The tetrahedral arrangement for 4-covalent non-metals such as
C, N, P and B is well established on various grounds, particularly that

of resolution into optically active forms. In like manner the tetrahedral disposition of the valency directions for Be in beryllium benzoylpyruvate [1] is shown by the resolution of this substance (I), the attachment of two

I.

$$\text{Ph}\diagup\text{C—O}\diagdown\text{Be}\diagdown\text{O—C}\diagup\text{Ph}$$

(structure I: two chelate groups, each with CH, C=O, CO₂H, coordinated to central Be)
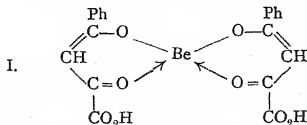
identical but non-symmetrical chelate groups conferring the necessary asymmetry on the molecule. The evidence for the tetrahedral form of the corresponding Zn and Cu compounds is much less conclusive. The non-planar arrangement of the beryllium valency directions is also well shown by a study of the crystal structure [2] of basic beryllium acetate, $Be_4O(CH_3COO)_6$. This substance crystallises in octahedra and behaves as a non-polar substance, being soluble in organic solvents. The investigation showed that the O atom is situated at the centre of a tetrahedron, with Be at each corner and an acetate group spanning each edge. Pauling and Sherman [3] showed that there are four mols. in each crystal cell, containing four BeO_4 tetrahedra with a common corner.

A planar configuration for some 4-co-ordinated metallic compounds has for a long time been assumed, e.g. for $[Pt(NH_3)_2Cl_2]$ (see p. 338). Tellurium was also considered to be planar in $Te(CH_3)_2I_2$ which can be obtained in a red and a green form [4] as follows :

(reaction scheme:)

$$\underset{\text{red, trans-}}{\overset{\displaystyle I}{\underset{\displaystyle I}{CH_3\text{—Te—}CH_3}}} \quad \overset{\text{Ag}_2\text{O + water}}{\underset{\text{HI}}{\rightleftharpoons}} \quad \overset{\displaystyle OH}{\underset{\displaystyle OH}{CH_3\text{—Te—}CH_3}} \quad \overset{\text{Dehydrate}}{\underset{\text{Heat in vacuo}}{\longrightarrow}}$$

$$\underset{CH_3}{\overset{CH_3}{>}}Te=O \quad \overset{\text{HI}}{\longrightarrow} \quad \underset{\underset{\text{green, cis-}}{\displaystyle I}}{\overset{\displaystyle \dot{C}H_3}{CH_3\text{—Te—}I}}$$
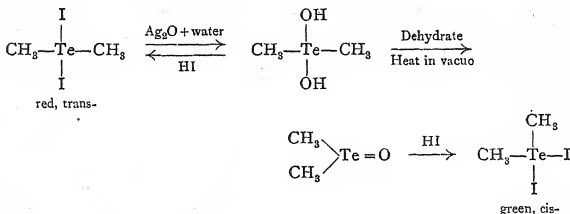
But it was shown later [5] that the dehydration is a much more complex process, involving a change somewhat of the pinacol-pinacolin type, i.e.

[1] Mills and Gotts, J. Chem. Soc., 1926, 3121.

[2] Bragg and Morgan, Proc. Roy. Soc., 1923, A 104, 437 ; Morgan and Astbury, ibid., 1926, A 112, 441.

[3] Proc. Nat. Acad. Sci., 1931, 20, 340.

[4] Vernon, J. Chem. Soc., 1920, 107, 86, 889.

[5] Drew, J. Chem. Soc., 1929, 560.

$$2CH_3-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Te}}-CH_3 \xrightarrow{-2H_2O} CH_3\underset{CH_3}{\overset{CH_3}{>}}Te\underset{O}{\overset{O}{<}}Te\underset{CH_3}{\overset{CH_3}{<}} \longrightarrow (CH_3)_3Te-O-Te\underset{CH_3}{\overset{O}{<}}$$
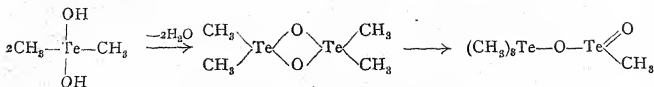
for on treatment with halogen acids, this yielded $(CH_3)_3TeI$ (or Br) and

$CH_3-Te\overset{O}{\underset{OH}{<}}$ which with further acid gave CH_3TeI_3 (or Br_3). The

green form is obtained by mixing these materials and is therefore a
dimeride $(CH_3)_3TeI$, CH_3TeI_3 and not a stereoisomeride of the red
substance; this view is further supported by the formation of mixed
types such as $(CH_3)_3TeI$, CH_3TeBr_3 for the reaction might proceed

$$(CH_3)_3TeI + CH_3TeI_3 \longrightarrow 2(CH_3)_2TeI_2 \text{ and } (CH_3)_3TeI + CH_3TeBr_3 \longrightarrow$$
$$(CH_3)_2TeIBr + (CH_3)_2TeBr_2$$
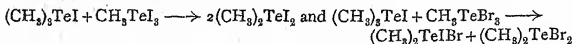
But each product is homogeneous and not separable into two products
as required in the second possible reaction.

The two forms of $Co(NH_3)_2Cl_2$ (pink and blue) formed by heating
$Co(NH_3)_6Cl_2$ under different conditions, were also formulated as cis-
and trans-planar forms by Biltz and Fetkenheuer[1] but there is no
substantial evidence in support of this view. Recently, however, the
α- and β-forms of dipyridinocobaltous chloride have been examined.[2]
The molecular weight of each in phenol and chloroform agrees with the
simple molecular form $CoCl_2 2py$, and X-ray analysis of the α-form
showed that the four groups must be coplanar with the Co, and that
it is a trans-form; the structure of the β-form could not be determined.
Dipyridinomanganous chloride was similarly shown to have a planar
structure. The ions $[MnO_4]'$ and $[MnO_4]''$ are both tetrahedral, which
serves to show that the primary valency of the co-ordinated atom,
as well as the nature of the attached groups, has an effect in determining
the spatial arrangement.

Cobalt is the basis of a tetrahedral structure, for example, in
Cs_3CoCl_5, which was shown by Powell and Wells[3] by X-ray analysis to
consist of $Cs_3^{+1}[CoCl_4]^{-2}Cl^{-1}$ and the grouping $[CoCl_4]''$ is tetrahedral; this
mixed type of formulation finds a counterpart[4] in $(NH_4)_3^{1+}[ZrF_6]^{2-}F^{1-}$
(see p. 329).

In 1931, Pauling,[5] from quantum mechanical considerations, predicted
that certain transition elements of co-ordination number 4 would give
stable tetrahedral configurations if the electrons from the first two
subgroups only (s and p) of the outer level were used to form the

[1] Z. anorg. Chem., 1914, 89, 97.
[2] Cox, Shorter, Wardlaw and Way, J. Chem. Soc., 1937, 1556.
[3] J. Chem. Soc., 1935, 359.   [4] Hessel and Mark, Z. Physik, 1924, 27, 89.
[5] J. Amer. Chem. Soc., 1931, 53, 1367.

valency bonds. If, however, one or more of the electrons used in binding comes from the d group of the incomplete inner level, the four covalencies may be distributed in a plane. A plane arrangement should therefore be met with in compounds of Ni, Pt and Pd—possibly but not necessarily exclusively. These predictions have been supported experimentally in at least four ways[1] :—

1. *X-ray Analysis*, by which the co-ordinated groups have been shown to be co-planar with the metal atom in the following compounds :

$K_2[PtCl_4]$ . . .	.	Dickinson, *J. Amer. Chem. Soc.*, 1922, 44, 774, 2404.
$K_2[PdCl_4]$ . . .	.	,, ,, ,,
$[Pt(NH_3)_4]Cl_2H_2O$.	.	Cox, *J. Chem. Soc.*, 1932, 1912.
$[Pt(NH_3)_4]PtCl_4$.	.	Cox, Pinkard, Wardlaw and Preston, *J. Chem. Soc.*, 1932, 2527.
$[Pd(NH_3)_4]PdCl_4$.	.	Drew, Pinkard, Preston and Wardlaw, *ibid.*, 1932, 1895.
$[Pden_2]Cl_2$. . .	.	Cox and Preston, *ibid.*, 1933, 1089.
$[Pd(NH_3)_4]Cl_2H_2O$.	.	,, ,,
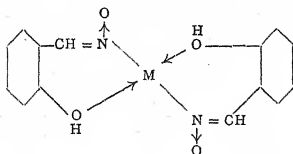
X-ray analysis showed this compound to have a centre of symmetry and therefore trans-planar configuration —Cox, Pinkard, Wardlaw and Webster, *J. Chem. Soc.*, 1935, 459.

(where M is Ni, Pd, Pt; or may be formulated as on p. 288).

A most complete examination by X-rays was made of the double thio-oxalates of potassium with nickel, palladium and platinum :
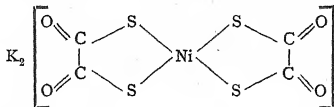
Not only was the symmetry of the molecules determined but the complete structure was elucidated by means of intensity measurements made possible by the scattering power of the K and S atoms being comparable with that of the other metal atom. The results showed conclusively that all four atoms of the complex ion are co-planar.

The compounds of Cu^{II} with acetylacetone and benzoylacetone of co-ordination number 4 were shown by Cox and Webster[2] by X-ray analysis to be planar.

X-ray analysis of the phthalocyanines[3] shows that the metal atom

---

[1] Exceptions to Pauling's predictions are known in some co-ordination compounds of bivalent copper, which have planar configurations.

[2] *J. Chem. Soc.*, 1935, 731.

[3] Robertson, *J. Chem. Soc.*, 1935, 615; 1936, 1195; Linstead and Robertson, *ibid.*, 1936, 1736.

(Cu, Ni, Pt, Be, Mn, Fe and Co) and the four surrounding *iso*indole nitrogen atoms are co-planar.
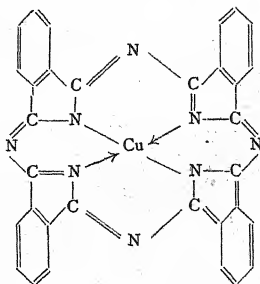
The particular groupings present in this assemblage of ring systems may have the effect of distorting the usual valency directions of the metal, for example, beryllium is usually tetrahedral.

Further, the compound $Pt(CH_3)_3Cl$, containing quadrivalent platinum was shown by X-ray analysis to be tetrahedral.[1]

2. *By the Isolation of Cis- and Trans- Forms.*—Evidence of this kind is obtained from the existence of unsymmetrical glyoximes in two varieties. Thus the two varieties of benzylmethylglyoxime[2] melt at 75-77° (cis, I), and 168° (trans, II).
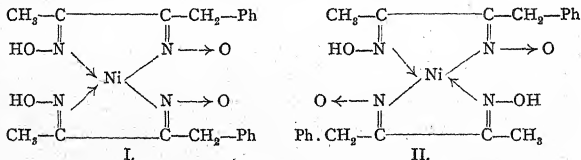
This type of isomerism is only possible if the four valency directions of the nickel are co-planar. The two forms are separated by taking advantage of their different solubilities in cold acetone, and the corresponding methyl *n*-propyl and *n*-butyl glyoximes have been similarly separated.[3]

Palladium benzylmethylglyoximes have also been obtained in two

[1] Cox and Webster, *Z. Krist.*, 1935, **A 90**, 561.

[2] Sugden, *J. Chem. Soc.*, 1932, 246.

[3] Cavell and Sugden, *J. Chem. Soc.*, 1935, 621.

varieties[1] and palladium and platinum complexes with glycine also exist in cis- and trans- varieties.[2]

$$
\begin{array}{ccc}
\text{OC}\!-\!\!-\!\text{O} & \text{O}\!-\!\!-\!\text{CO} \\
| & \quad\quad>\!\text{Pt}\!<\quad\quad | & \text{and} \\
\text{CH}_2\!-\!\text{NH}_2 & \text{NH}_2\!-\!\text{CH}_2
\end{array}
\qquad
\begin{array}{c}
\text{OC}\!-\!\!-\!\text{O}\qquad\qquad \text{NH}_2\!-\!\text{CH}_2 \\
\quad\quad>\!\text{Pt}\!<\quad\quad \\
\text{CH}_2\!-\!\text{NH}_2\qquad\qquad \text{O}\!-\!\!-\!\text{CO}
\end{array}
$$
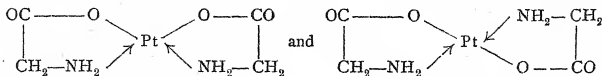
Drew and Head[3] prepared

$$
\left[
\begin{array}{c}
\text{H}_2\text{C}\!-\!\text{NH}_2\qquad\qquad \text{NH}_3 \\
\qquad\qquad\searrow\text{Pt}\swarrow \\
(\text{CH}_3)_2\text{C}\!-\!\text{NH}_2\qquad\qquad \text{NH}_2 . \text{C}_2\text{H}_5
\end{array}
\right] \text{Cl}_2 \text{ in cis- and trans- forms}
$$

and also

$$
\left[
\begin{array}{c}
\text{H}_2\text{C}\!-\!\text{NH}_2\qquad\qquad \text{NH}_2\!-\!\text{CH}_2 \\
\qquad\qquad\searrow\text{Pt}\swarrow \\
(\text{CH}_3)_2\text{C}\!-\!\text{NH}_2\qquad\qquad \text{NH}_2\!-\!\text{C}(\text{CH}_3)_2
\end{array}
\right] \text{Cl}_2
$$
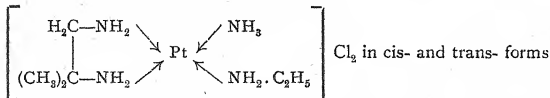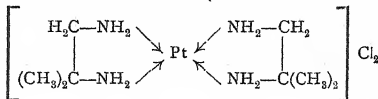
The second compound is particularly interesting in view of its reported resolution by Reihlen and Hühn (see p. 354).

3. *By Measurements of Magnetic Susceptibility.*—Paramagnetism appears when the electron shells are incomplete and contain an unpaired electron. The *d*-electrons are chiefly responsible for the magnetic moment of the atom, and sharing of them should reduce the paramagnetism so that planar 4-covalent nickel compounds, for example, should be diamagnetic; the benzylmethylglyoximes are diamagnetic, and measurements of their dipole moments also support the planar structure. James[4] measured the magnetic susceptibilities of all the more important 4-co-ordinated palladium compounds, and his results support the planar distribution.

4. *By Resolution into Optically Active Forms.*—The resolution of

$$
\left[
\begin{array}{c}
\text{H}_2\text{C}\!-\!\text{NH}_2\qquad\qquad \text{NH}_2\!-\!\text{CH} . \text{C}_6\text{H}_5 \\
\qquad\qquad\searrow\text{Pt}\swarrow \\
(\text{CH}_3)_2\text{C}\!-\!\text{NH}_2\qquad\qquad \text{NH}_2\!-\!\text{CH} . \text{C}_6\text{H}_5
\end{array}
\right] \text{Cl}_2
$$
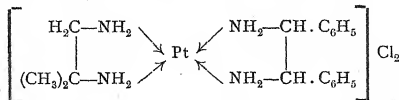
by Mills and Quibell[5] is particularly noteworthy in this connection. This compound was prepared by treating *iso*butylenediamine with

[1] Dwyer and Mellor, *J. Amer. Chem. Soc.*, 1935, 57, 605.

[2] Grünberg and Ptizyn, *J. prakt. Chem.*, 1933, ii, 136, 143; Pinkard, Sharratt, Wardlaw and Cox, *J. Chem. Soc.*, 1934, 1012.

[3] *J. Chem. Soc.*, 1934, 221.   [4] *J. Amer. Chem. Soc.*, 1935, 57, 471.

[5] *J. Chem. Soc.*, 1935, 839.

potassium chloroplatinite and the resulting compound was brought into reaction with stilbene diamine (*i.e.* the meso, inactive form) to give the product above.

$$
\begin{array}{c}
H_2C\text{---}NH_2 \\
| \\
(CH_3)_2C\text{---}NH_2
\end{array}
\quad + \quad K_2PtCl_4 \quad \longrightarrow \quad
\begin{array}{c}
H_2C\text{---}NH_2 \\
\diagdown \\
\diagup \quad PtCl_2 \\
(CH_3)_2C\text{---}NH_2
\end{array}
$$
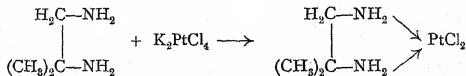
The preparation of this compound was designed to afford a crucial test between the planar and tetrahedral configurations. The cation will be dissymmetric if the platinum valencies lie in one plane:
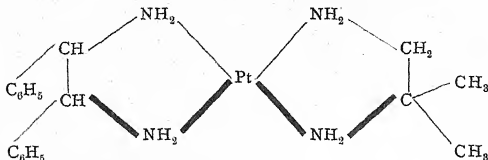
If, however, the platinum valencies have a tetrahedral arrangement, the molecule will possess a plane of symmetry, for the plane of symmetry of the diphenylated ring will then coincide with the plane of the dimethylated ring and become a plane of symmetry of the whole ion. The salts were resolved by means of diacetyltartaric acid and showed a high degree of optical stability.

In contrast with this case, some of the evidence for a tetrahedral distribution is not particularly well-established. Reihlen and Hühn,[1] for example, resolved [Pt(isobutylenediamine)$_2$]Cl$_2$. Drew and Head (see p. 353), however, obtained this material in well-defined cis- and trans- forms, and Drew, Head, and Tress[2] prepared the α-bromo-*d*-camphor-π-sulphonates of each in a well-crystallised condition, but failed to effect separation into optically active varieties. The optical activity observed by Reihlen and Hühn was small and may have been due to impurities. On the other hand, Drew, Head and Tress failed to resolve

$$
\left[
\begin{array}{c}
H_2C\text{---}NH_2 \\
| \\
(CH_3)_2C\text{---}NH_2
\end{array}
\diagup\!\!\!\!\!\searrow Pt \diagdown\!\!\!\!\!\swarrow
\begin{array}{c}
NH_2\text{---}CH_2 \\
\diagdown CH\cdot CH_3 \\
NH_2\text{---}CH_2
\end{array}
\right] Cl_2.
$$
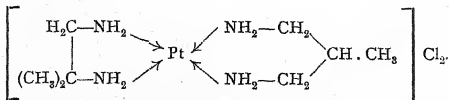
This should be resolvable on a planar, but not on a regular tetrahedral basis of the valency distribution about platinum.

[1] *Annalen*, 1931, 489, 42 ; 1932, 499, 144. See also Rosenheim and Gerb, *Z. anorg. Chem.*, 1933, 210, 289.

[2] *J. Chem. Soc.*, 1937, 1549.

Halides of the Quinque-, Sexa- and Octa-valent Metals

These compounds are devoid of any saline character, and cannot be prepared by the action of the acid on the metallic oxide. The synthetic method of preparation from the free halogen and the metal (or mixture of the oxide with carbon) is useful, provided a high temperature is employed. Halides of the non-metals, *e.g.* CCl_4, S_2Cl_2, PCl_5, can also be used to attack the oxides of these metals. The fluorides can be made by Ruff's method—by decomposing the chlorides with anhydrous hydrofluoric acid. Iodides, which even with metals of lower valency show a great tendency to decompose, are exceptional in this group, but TaI_5 (m.pt. 365°) and NbI_5 have been prepared.[1]

These halides hydrolyse with the greatest facility; all except tungsten hexachloride fume in the air, deliquesce and hiss vigorously when poured into water, when the hydroxide of the metal is formed, although it is not always precipitated at once. They are soluble in solvents which themselves contain halogens (CCl_4, S_2Cl_2) without decomposition, and in consequence of the high halogen content of these metallic compounds, melting and volatilisation occur at low temperatures. They can be distilled unchanged in an atmosphere of the halogen and the vapours show normal density. The melting and boiling points are not as a rule very far apart, and the melting point of UF_6 at atmospheric pressure lies above the boiling point.

The following tables give the melting and boiling points of the more important compounds of this class (*cf.* also the halides of quinquevalent Sb, p. 745 *et seq.*):

I. Quinquevalent Metals

		F_5.	Cl_5.	Br_5.
V	Boiling point	112·2°	...	...
		White	...	...
Nb	Melting point	72°	212°	Ca. 150°
	Boiling point	236°	240·5°	270°
		Colourless cryst.	Yellow needles	Dark red powd.
Ta	Melting point	96·8°	211·3°	240°
	Boiling point	229·5°	242°	320°
		Colourless cryst.	Yellow	Yellow cryst.
Mo	Melting point	...	194°	...
	Boiling point	...	268°	...
			Dark violet cryst.	...
W	Melting point	...	248°	276°
	Boiling point	...	275·6°	333°
			Black needles	Black violet.
U	...	...	Dark needles easily dissociating into UCl_4 and Cl	...
Ru	Melting point	101°	...	...
	Boiling point	Ca. 272°	...	...
		Dark green transparent cryst.		

[1] Körösy, *Technikai Kurir*, 1939, 9, 81.

II. Sexavalent Metals

		F_6.	Cl_6.	Br_6.
Mo	Melting point	17°	...	...
	Boiling point	35°	...	...
		White cryst.	...	...
W	Melting point	2°	275°	?
	Boiling point	19·5°	346°	?
		Colourless	Dark violet	Bluish black needles.
U	Melting point	69·2° (2 atm.)	...	...
	Boiling point	56·2° (sublimes)	...	...
		Colourless	...	...

The octafluoride of osmium is of special interest, being the highest metal halide known. Whereas palladium gives a trifluoride, platinum and rhodium tetrafluorides, ruthenium a pentafluoride and iridium a hexafluoride as the compound richest in halogen, osmium forms an octafluoride when heated in fluorine; a tetra- and hexa-fluoride are simultaneously formed. The octafluoride is a lemon yellow solid melting at 34·4° to a liquid which boils at 47·5°. The vapour begins to decompose slowly at 225° and the dissociation becomes rapid above 400°. It is decomposed by water and compounds are formed with alkali fluorides. This compound opens up many questions of valency not yet solved satisfactorily; it may contain single electron bonds but duplet linkages, involving a valency shell of sixteen electrons, appear to be much more probable.

When the vapour of the halide is passed over the oxide, or when the oxide is not completely halogenated, compounds containing both oxygen and halogen are obtained, the oxyfluorides being formed by treating the oxychlorides with dry hydrofluoric acid (Ruff). Most of the oxyhalides can be distilled unchanged, and are so easily hydrolysed that they fume in the air and hiss when added to water. The following are the most important:

I. Quinquevalent metals

	Melting Point.	Boiling Point.	
VOF_3	Ca. 300°	480°	Yellowish white incrustations.
$VOCl_3$	18°	127°	Pale yellow liquid.
$NbOF_3$	?	?	Cryst.
$NbOCl_3$	?	Sublimes 400°	White silky cryst.
$NbOBr_3$	...	Sublimes undecomp. in Br_2	Pale yellow.
$MoOCl_3$	< 100°	< 100°	Dark green cryst.

II. Sexavalent metals

$MoOF_4$	97°	180°	White.
MoO_2F_2	...	Subl. > 271°	White.
MoO_2Cl_2	...	...	Yellowish white.
MoO_2Br_2	...	...	Yellowish red.
WOF_4	110°	190°	White scales.
$WOCl_4$	210°	227·5°	Red needles.
WO_2Cl_2	266°	Little > 266°	Orange yellow flakes.
$WOBr_4$	277°	327°	Brownish black needles.
WO_2Br_2	...	...	Brassy scales.

The uranyl halides are essentially different from these oxyhalides; the radical $UO_2^{\cdot\cdot}$, which occurs, for example, in UO_2F_2, UO_2Cl_2 and UO_2Br_2, forms true salts with acid radicals which are known as the uranyl salts. They are yellowish green in colour and hydrolyse only to a slight extent in aqueous solution; they can be made from the oxide and the halogen acid, and crystallise readily, often with water of crystallisation. They are further discussed on p. 490.

The halides of the quinquevalent metals form complex salts with the halides of other metals in much the same way as those of quadrivalent metals. These complexes are formed when alkali halide is added to a solution of the oxide of the metal in the halogen acid; they are not hydrolysed nearly as much as the halides themselves in solution. The fluorides are the most important, and those of niobium and tantalum are useful in the isolation and characterisation of the metals, e.g. $K_2[TaF_7]$ (Marignac). It is notable that an apparent co-ordination number 7 is common in these compounds, although it is seldom found as a general rule (cf. $M_2[NbF_7]$; $TaCl_5 . 2C_5H_5N$), but it may only be 6 (see pp. 303 and 350). Eight also appears as co-ordination number in these complexes, e.g. $M_3[TaF_8]$. In the presence of less concentrated acid, oxyhalogen salts are formed, e.g. $M_2[NbOCl_5]$, $M_2[NbOBr_5]$,* $M[NbO_2F_2]$, $M_3[TaOF_6]$, $M_2[\overset{v}{Mo}OF_5]$, $M[\overset{vi}{Mo}O_2F_3]$, $M_2[\overset{vi}{Mo}O_2Cl_4]$, etc. These compounds are but briefly referred to here, but they are related to the halogenoantimoniates $M[SbCl_6]$, the halogenochromates, the fluophosphates, fluoselenates, fluoriodates and other halogenated salts of true acids, which will be dealt with later. Complex compounds of bivalent tantalum and niobium have also been described, e.g. $3Ta(Nb)Cl_2 . HCl . 4H_2O$ which is formulated $H[(Ta, Nb)_3Cl_7H_2O]3H_2O$. The compounds $Mo_3Cl_6 . HCl . 4H_2O$ and $W_3Cl_6 . HCl . 4H_2O$ have also been prepared.

* Weinland and co-workers, *Z. anorg. Chem.*, 1905, 44, 81 ; 1907, 54, 114.

OXYGEN COMPOUNDS OF THE HALOGENS

Constitution—Halogen monoxides and the hypohalites—Chlorates, bromates and iodates—Chlorine dioxide and chlorites—Perchloric acid—Periodic acid—Basic compounds of iodine—Compounds of the halogens with one another

THE oxygen compounds of the halogens are given in the following table:

OF_2	Cl_2O	$HClO$	Br_2O	$HBrO$		HIO
O_2F_2		$HClO_2$	$(Br_3O_8)_n$			
OF						
$? HFO_3$	ClO_2	$HClO_3$	BrO_2	$HBrO_2$	I_2O_4	HIO_3
	Cl_2O_6				I_2O_5	
	Cl_2O_7	$HClO_4$			I_4O_9	H_5IO_6
	(ClO_4)				$(IO_4)x$	

The discontinuity of the foregoing table is noteworthy. The halogens give rise to analogous compounds in the series $HClO$—$HBrO$—HIO and $HClO_3$—$HBrO_3$—HIO_3. There is no chlorine or iodine compound corresponding to Br_3O_8, and even when the chlorine and iodine compounds have comparable formulae the similarity is confined to the empirical composition, and they differ in chemical properties. Perchloric and periodic acids differ in hydration and also in other respects to such an extent that it is obvious that the structure of the two compounds is not analogous. Similarly, I_2O_4 does not correspond to polymerised chlorine dioxide, and is one of the compounds in which iodine has basic properties (see p. 385).

Constitution.—The oxides Cl_2O, Br_2O, Cl_2O_7 and I_2O_5 can be considered as the anhydrides of the corresponding acids, as they are converted into the latter on addition of water and can be made from the acids by dehydrating them. There are, however, no acids corresponding to the oxides of fluorine, or to ClO_2 and I_2O_4, and when chlorine dioxide forms salts a double reaction ensues, giving equivalent quantities of chlorate and chlorite (*cf.* NO_2). The oxides $(ClO_4)_n$, Cl_2O_6 and Br_3O_8 behave in a similar manner.

$$2ClO_2 + H_2O \longrightarrow HClO_2 + HClO_3$$
$$Cl_2O_6 + H_2O \longrightarrow HClO_3 + HClO_4$$
$$(ClO_4)_2 + H_2O \longrightarrow HClO_4 + HClO_5$$
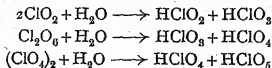
The electronic formulae of the oxides have not been established with certainty but some undoubtedly contain odd or single electron linkages, *e.g.* ClO_2. Cheesman[1] considers that of the eleven possible ways of formulating this oxide the following two fit the parachor values best:
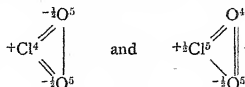
The constitution of these compounds was formerly explained by the assumption that chlorine showed a variable primary valency ranging from the value one in hypochlorous acid and increasing by two units with each additional oxygen atom:
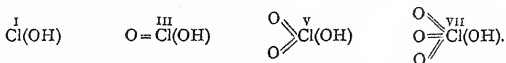
It is, however, equally reasonable to assume that the chlorine is univalent throughout, and the oxygen is linked by secondary valencies.

Measurement of interatomic distance in the ClO_2 molecule indicates that the normal structure is a hybrid involving resonance of a *three-electron* bond between the two Cl—O positions:
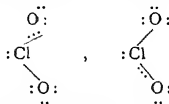
The *three-electron bond* (*cf.* the one-electron bond, is believed to be responsible for the stability of the helium molecule ion, He_2^+, which may be regarded as $He \cdots He^+$. It also occurs in other molecules (*e.g.* NO, NO_2, O_2^-, etc.).

The electronic formulae of the chlorine acids are an interesting series:

$$H = O^4 = Cl^6 \qquad i.e. \qquad H—O—Cl$$

$$H = O^4 = \overset{+}{Cl}^4 = \bar{O}^6 \qquad i.e. \qquad H—O—Cl \rightarrow O$$

$$H = O^4 = \overset{++}{Cl}^2 \overset{\nearrow \bar{O}^6}{\underset{\searrow \bar{O}^6}{}} \qquad i.e. \qquad H—O—Cl \overset{\rightarrow O}{\underset{\rightarrow O}{}}$$

$$H = O^4 = \overset{+++}{Cl} \overset{\nearrow \bar{O}^6}{= \bar{O}^6} \qquad i.e. \qquad H—O—Cl \overset{O}{\underset{\searrow O}{\underset{\nearrow \rightarrow O}{}}}$$
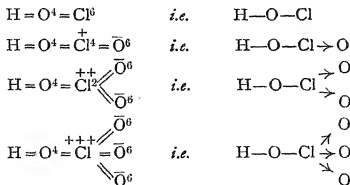
With the formation of perchloric acid, the lone electron pairs, which are present in the acids containing less oxygen, are completely shared and as chlorine does not tend to form electron shells larger than the octet,

[1] *J. Chem. Soc.*, 1930, 35.

perchloric acid represents the final stage of oxygen addition.   The ions, all univalent, may be written:

$$
\begin{array}{ccccc}
& & & & :\overset{\cdot\cdot}{O}: \\
& & & :\overset{\cdot\cdot}{O}: & :\overset{\cdot\cdot}{O}:\overset{\cdot\cdot}{Cl}:\overset{\cdot\cdot}{O}: \\
\overset{\cdot}{:}\overset{\cdot\cdot}{Cl}: & :\overset{\cdot\cdot}{O}:\overset{\cdot\cdot}{Cl}: & :\overset{\cdot\cdot}{O}:\overset{\cdot\cdot}{Cl}:\overset{\cdot\cdot}{O}: & :\overset{\cdot\cdot}{O}:\overset{\cdot\cdot}{Cl}:\overset{\cdot\cdot}{O}: & :\overset{\cdot\cdot}{O}: \\
Cl'\ ion & ClO'\ ion & ClO_2'\ ion & ClO_3'\ ion & ClO_4'\ ion
\end{array}
$$
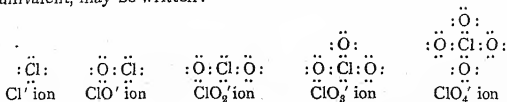
The distribution of the electrons is probably different in the salts and in the free acids—the acids are non-polar and the salts are polar as explained below.

Pauling's view of the ClO_3^- ion is:

$$
\left[
\begin{array}{c}
:\overset{\cdot\cdot}{O}:^- \\
| \\
:\overset{++}{Cl}\text{—}\overset{\cdot\cdot}{O}:^- \\
| \\
:\overset{\cdot\cdot}{O}:^-
\end{array}
\right]^-
$$
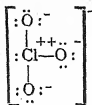
Although interatomic distances indicate a large amount of double-bonded character in the Cl—O bonds, bond angles are close to those expected for single bonds.   The chlorite ion, ClO_2^- may be regarded as resonating between structures like

$$
\begin{array}{ccc}
:\overset{\cdot\cdot}{O}:^- & & :\overset{\cdot\cdot}{O}:= \\
/ & & / \\
:\overset{}{Cl}^+ & , & :\overset{}{Cl}^+ \\
\backslash & & \backslash\backslash \\
:\overset{\cdot\cdot}{O}:^- & & O:
\end{array}
, \text{ etc},
$$
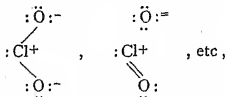
since again there is evidence of double-bonded character in the Cl—O bonds.

Schafer[1] and Hantzsch[2] have published considerable work on the constitution of these compounds by a consideration of their ultra-violet absorption spectra.   Hantzsch had previously shown that the spectrum of a compound is not markedly altered by the substitution of an optically indifferent radical, provided the main structure is not affected.   Thus, for example, the different salts of a given acid all have much the same spectrum when the metal is strongly electro-positive and does not itself affect the spectrum.   Even when the salts are dissociated electrolytically there is no great change.   On the other hand, the spectrum suffers a profound alteration if the mode of attachment is changed.   This effect can be observed in organic acids when salts or esters are made from them.   The spectra of ester and salt are different throughout, while that of the acid is intermediate between the other two.   The structure of the free acid should also, therefore, be intermediate between that of salt and that of ester. Hantzsch, using the classical ideas on valency, considered that in the ester the alkyl group is attached through one oxygen atom to the central carbon atom (I), while in the salts both O atoms of the carboxyl group are attached in some way to the metal atom (II):

$$
\text{I.}\quad R\cdot C \begin{array}{c} \diagup O \\ \diagdown O\text{—}CH_3 \end{array}
\qquad\qquad
\text{II.}\quad R\cdot C \begin{array}{c} \diagup O \\ \diagdown O \end{array} M
$$
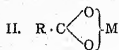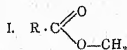
[1] Z. anorg. Chem., 1916, 97, 285 ; 98, 70 ; Z. physikal. Chem., 1919, 93, 312.
[2] Ber., 1917, 50, 1422.

In the first compound the CH_3 radical is in the same sphere as the oxygen, and there is thus a close connection between them ; in the second formula the metal atom is in the outer sphere, not attached to any definite atom, but is in a loose relation to several. It can be ionised when in this position. Both formulae are representations of extreme positions, and in most compounds the two forms are in equilibrium and both kinds of molecules exist together. According to Hantzsch, this occurs to a notable extent in the acids, as indicated in the formulae :

I. R·C$\underset{\text{OH}}{\overset{\text{O}}{<}}$ $\rightleftharpoons$ II. R·C$\underset{\text{O}}{\overset{\text{O}}{<}}$H.

Pseudo-acid.   True acid.

The solvent determines which form is in excess, and thus in ether (I) preponderates, in water (II), and the spectra indicate that form (I) is analogous to that of the ester and (II) to that of the salts. The H atom in (I) cannot form an ion any more than the Cl atoms in the complex $\left[Cr \genfrac{}{}{0pt}{}{Cl_2}{(H_2O)_4} \right]^{\cdot}$, while in (II) the H atom is dissociated in just the same way as the Cl atoms in $[Cr(H_2O)_6]Cl_3$. The other typical acid reactions also belong exclusively to the form II.

These arguments for organic acids hold equally for all oxyacids. Schafer was able to show that the spectra of free hypochlorous and hypobromous acids are similar to that of the esters, but entirely different from those of the salts. Thus the formulae of the acids are of the pseudo form (I), in which the H atom is closely attached to the other atoms, while that of the salts is of type II :

I. $\left[Cl \genfrac{}{}{0pt}{}{:O}{\cdot\cdot\cdot H} \right]$.   II. $\left[ClO \right]^{I} M$.

These might be written $Cl^6=O^4=H$ or $H=\overset{+}{Cl}{}^4=\overset{-}{O}{}^6$ and $[Cl^6=O^6]^{-}\overset{+}{M}$ but resonance effects would lead to a formulation such as I.

If the hydrolysis of the salt is augmented the spectrum changes, as free acid is then formed. The differing structure of the free acid and the salts accounts for their different chemical behaviour.

The structure of the hypo-acids is in all probability reflected in the higher oxyacids, and thus the following formula can be assumed for the chlorates : $Cl\genfrac{}{}{0pt}{}{O}{<O}{O}M$.

Hantzsch, however, now considers[1] that the ionised (polar) form, hitherto regarded as the " true acid " form does not exist as such until it is dissolved and has added on water (see p. 222).

Fluorine, Chlorine and Bromine Monoxides and the Hypo-Acids

All the compounds of chlorine and oxygen can be made from chlorine monoxide, so that compound will be discussed first. It is a strongly endothermic substance, $Cl_2 + O = Cl_2O - 17.9$ Cals., so that it is unlikely that it would be possible to synthesise it from its elements. When, however, it is formed as a by-product in a reaction which is strongly exothermic, there is often enough energy to cover that taken up in the formation of the Cl_2O. The interaction of chlorine with dry mercuric oxide is an example of such a reaction, the formation of

[1] E.g. Ber., 1927, 60, 1933.

mercuric chloride being strongly exothermic, and hence $HgO + 2Cl_2$ $= HgCl_2 + Cl_2O$. The reaction takes place in the cold, and a brownish-yellow gas is produced, not much darker than chlorine. It can be condensed to a brownish-red liquid at $2°$, freezing at $-116°$, and has a smell intermediate between those of chlorine and iodine.

This compound decomposes explosively on very slight stimulation, though in the gaseous state the explosion is fairly mild. The introduction of a hot wire into the gas, or local heating due to any chemical reaction, causes decomposition, and as it is a powerful oxidising and chlorinating agent, the presence of a substance easily attacked in either way is sufficient (*e.g.* S, P, C, metals, H_2S, NH_3, and, in particular, organic substances like cork or stopcock grease). Bromine and iodine are oxidised by the gas without explosion. It is soluble in liquid sulphur dioxide to a considerable extent without reaction. The rates of decomposition in the gaseous state and in carbon tetrachloride solution are about the same at the same temperature.

The gas dissolves readily in water (200 vols. in one of water at $0°$), giving an orange liquid. This high solubility indicates compound formation and hypochlorous acid is produced, though the colour is partly due to free Cl_2O in the liquid, for on distillation the first fractions are richer in the gas and of very deep colour. The acid can of course be produced direct if the oxide is made in presence of water, as, for example, when mercuric oxide is suspended in water and a stream of chlorine passed through the liquid.

Small quantities of a volatile oxide of bromine, Br_2O, have been obtained[1] by the interaction of HgO with Br_2 in carbon tetrachloride solution. It is also formed by the slow decomposition of bromine dioxide (p 377). It smells like hypochlorous acid and melts to a deep brown liquid at $-17.5°$. With sodium hydroxide, the hypobromite is formed. The solution is stable in the dark at $-20°$ but decomposes in light or at room temperature forming oxygen, chlorine, bromine and phosgene.

Hydrolysis of the Halogens.—The reaction of chlorine with water proceeds as follows: $Cl_2 + HOH \rightleftharpoons ClOH + HCl$. This hydrolysis of the chlorine is very incomplete, for the equilibrium lies well to the left, and hypochlorous acid is only formed in any quantity when the HCl is removed by being converted into a non-ionised product. That is why HgO is used in the usual preparation, for the $HgCl_2$ is only slightly ionised (*cf.* p. 268), and if cupric oxide is used instead, the reaction does not go forward. Silver oxide can be employed as the chlorine ions are removed as insoluble AgCl.

As a rule, however, the reaction is favoured by removing the Cl and H ions at the same time by working in alkaline solution, the

[1] Zintl and Reinäcker, *Ber.*, 1930, 63 B, 1098; Brenschede and Schumacher *Z. physikal. Chem.*, 1935, B 29, 356; *Z. anorg. Chem.*, 1936, 226, 370.

salts of the two acids being obtained. Thus when chlorine is passed into sodium hydroxide the reaction goes almost to completion; $Cl_2 + 2NaOH \longrightarrow ClONa + NaCl + H_2O$. If alkali carbonate is used instead, the transformation is also complete, as the chlorine reacts in the first instance with the hydrolysed part of the salt, causing further hydrolysis until the carbonate is entirely converted into chloride and hypochlorite.

The position of equilibrium in the hydrolysis of chlorine has been determined by Jakowin,[1] who found the concentration of free chlorine by shaking solutions of chlorine in water with carbon tetrachloride. As the distribution coefficient of the chlorine is known, and the hypochlorous acid is insoluble in the solvent added, the concentration of the chlorine in the mixture can be found from that in the CCl_4. As the water is present in relatively great quantity it can be left out of account in calculating the equilibrium constant of the reaction $Cl_2 + H_2O \rightleftharpoons ClOH + HCl$, as the number of water molecules is not appreciably diminished. The HCl is dissociated into its ions, and thus the constant is $\dfrac{ClOH \times H^{\cdot} \times Cl'}{Cl_2} = K$.

The hydrolysis of bromine and iodine is similar in its general features, but the equilibrium lies further towards the left-hand side, and the quantities of hypo-acids formed are smaller. The equilibrium constants found experimentally are as follows:

$$\frac{ClOH \times H^{\cdot} \times Cl'}{Cl_2} = K = 4 \cdot 5 \times 10^{-4}; \quad \frac{BrOH \times H^{\cdot} \times Br'}{Br_2} = K = 5 \cdot 2 \times 10^{-9}; \quad \frac{IOH \times H^{\cdot} \times I'}{I_2} = K = 3 \times 10^{-13}.$$

They decrease in value from chlorine to iodine as the quantity of hypo-acid formed becomes less, but the yield of hypobromous and hypiodous acids can be increased by removing the free acids. This occurs if alkalis are present, or even if only the halogen ions are removed by addition of mercuric oxide or silver salts to the water; e.g. $AgNO_3 + I_2 + H_2O \longrightarrow AgI + HIO + HNO_3$.

The low hydrolysis constant of the bromine and iodine indicates the ready formation of free halogen from the two acids, an effect which can be observed even in the preparation of the alkali salts themselves. The reaction between equivalent quantities of chlorine and alkali hydroxide is practically complete, but with bromine and iodine it is to some extent reversible. As the hypo-acids are weak the alkali salts are hydrolysed, and the free acid thus formed gives the element on decomposition—more easily when the constant referred to above is lower. Excess of hydroxyl ions represses the hydrolysis of the salt, but the incompleteness of the original reaction is shown by the fact that free iodine can exist in alkaline solution. For example, solutions of potassium iodide oxidise in the air, turning yellow owing

[1] Z. physikal. Chem., 1899, 29, 613.

to liberation of free iodine, although the solution becomes alkaline at the same time. Hypoiodite is first formed, and the reaction by which it can be produced is reversed: $2KIO + H_2O \longrightarrow 2KOH + I_2$. The starch test for iodine can therefore be used in weakly alkaline solutions, though it fails when the solution is very alkaline, as the formation of hypiodite is then almost complete. The iodide can, however, be liberated from such an alkaline solution by the addition of bicarbonate as the OH ions are thus repressed to an extent which prevents the complete formation of hypiodite. The addition of iodide ions also brings back the colour of a starch iodine solution which has been bleached by the addition of alkali, owing to the equilibrium $\dfrac{I' \times H^{\cdot} \times HIO}{I_2} = K$, in which the quantity of free iodine is increased on addition of iodide ions, the HIO being used up.

The formation of hypiodous acid by the hydrolysis of nitrogen iodides is remarkable—

$$N_2I + H_2O \longrightarrow N_2H + HIO \text{ and } NI_3 + 3H_2O \longrightarrow NH_3 + 3HIO.$$
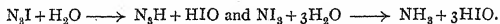
The hypo-acids can also be prepared by direct oxidation of the halides. Potassium iodide, as mentioned above, is oxidised in the air, and such oxidising agents as hydrogen peroxide, permanganate, and particularly fluorine, convert halogen hydrides into hypo-acids, but this method of formation has little practical application.

Properties of the Hypo-Acids.—These acids are not known in the anhydrous state; their aqueous solutions are formed when solutions of their salts are acidified, and hypochlorous acid can be distilled from the mixture. It is immaterial whether weak (CO_2) or strong acids (HNO_3) are used for acidifying. The stability of the hypobromous and hypiodous acids is of a much lower order than that of hypochlorous acid, and even if hypobromous acid is distilled under reduced pressure, solutions containing more than 1 per cent. cannot be obtained; the decomposition into bromine and bromic acids proceeds rapidly, and is complete at 60°. Hypiodous acid cannot be distilled at all.

Hypochlorous acid has a yellowish colour, while hypobromous acid is straw yellow and hypiodous acid is greenish yellow. The smell of the chlorine acid is rather like that of the free element, but less irritating; that of hypobromous acid is like jasmin, while hypiodous acid smells like saffron. The typical odours of the acids are also to be noticed in the salts, for a trace of free acid is always liberated by the carbon dioxide of the air. Hypochlorous acid is only about a tenth as strong as carbonic acid, hypobromous acid is weaker still, while hypiodous acid shows a slight basic tendency, for it dissociates amphoterically into $I^{\cdot} + OH'$ rather more than into $IO' + H^{\cdot}$. The strength of hypochlorous acid compared with carbonic acid was determined by J. Sand,[1]

[1] *Z. physikal. Chem.*, 1904, **48**, 60.

who compared the solubility of carbon dioxide in sodium hypochlorite with that in pure water. It was found that the former solubility was the greater, as the free alkali formed by hydrolysis combined with the carbon dioxide to form bicarbonate. The equilibria are thus

$$\frac{H^{\cdot} \times ClO'}{HClO} = k_{HClO} \qquad \text{and} \qquad \frac{H^{\cdot} \times HCO_3'}{(H_2O) \times CO_2} = k_{CO_2},$$
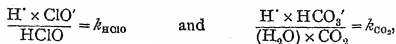
and hence, $\dfrac{ClO' \times CO_2}{HCO_3' \times HClO} = \dfrac{k_{HClO}}{k_{CO_2}}$, as the water can be assumed to undergo no change in quantity during the reaction. The constant k_{CO_2} is known from other experiments, so that k_{HClO} can be calculated from the increased absorption of the carbon dioxide in the hypochlorite solution.

The low strength of the hypo-acids, which reaches a minimum in HIO, causes their salts to be heavily hydrolysed in solution, even in the presence of hydroxyl ions. A secondary consequence is the formation of iodates in alkaline solution, for this transformation involves the production of free acids of greater strength than the hypiodous acid. The more basic character of the compound IOH is also indicated by the stability of ICl_3 and the hydrolysis of NI_3 into NH_3 and IOH. The latter reaction is exactly analogous to the hydrolysis of metallic nitrides with formation of the hydroxide of the metal. Nitrogen chloride cannot easily be hydrolysed in this manner, as the chlorine cannot assume the position which more positive elements occupy. The existence of negative IO' ions is, however, indicated by the tendency to form solid hypiodites, but so far none of these have been definitely characterised.

The hypochlorites are sufficiently hydrolysed to make it impossible to prepare the hypochlorites of heavy metals in the solid state—only the hydroxides are left on evaporation. When the hydroxide is soluble, as, for example, those of the alkali and alkaline earth metals, the equilibrium is preserved and the hydrolysis does not proceed to completion. In solutions of alkali hypochlorites of normal concentration it amounts to 0·052 per cent. at 25°, and thus the solutions smell of hypochlorous acid even if carbon dioxide is excluded.

Decomposition and Oxidising Action. — As the hypo-acids are strongly endothermic compounds they decompose very easily. The first result is the liberation of oxygen; but this then attacks the halogen hydracid formed at the same time, and thus free halogen is produced; thus

$$\begin{matrix} Cl:H \\ \\ Cl:H \end{matrix} + O:Cl:H.$$

It has been calculated that the reaction

$HClO \rightleftharpoons HCl + O$ would be reversed completely at an oxygen pressure of $10^{19 \cdot 25}$ atmospheres at 15°. This pressure is so enormous that HClO

should decompose under atmospheric pressure with extreme violence, and it is hardly feasible to explain its relative stability by the invocation of various retarding effects, as has been done; either the calculation or the explanation must be wrong. The decomposition proceeds slowly without stimulus, particularly in concentrated solution; the rate is increased on exposure to light, but is still easily measurable. Even with catalysts the decomposition is not violent, and a steady stream of oxygen can be obtained by warming a suspension of bleaching powder to which a few drops of a cobalt or nickel salt have been added. Carbon and phosphorus do not act as catalysts, nor, indeed, are they notably attacked.

In the second place, decomposition may occur by the oxygen from two molecules of hypochlorite becoming attached to another molecule

and thus forming chlorate; thus $\begin{array}{c} \text{O ClH} \\ \text{HClO} \\ \text{O ClH} \end{array}$. This reaction does

not occur between three ClO′ ions in accordance with the equation $3ClO' \longrightarrow ClO_3' + 2Cl'$, but according to Förster and Jorre[1] the presence of free hypo-acid is necessary: $ClO' + 2HClO \longrightarrow ClO_3' + 2H^\cdot + 2Cl'$. A trace of free acid is sufficient, as the $H^\cdot$ ions are continually set free, and actually the hydrolysis of the hypochlorite provides the necessary hypo-acid, though moderate addition of acid accelerates the reaction. The transformation occurs more readily in passing down the series from hypochlorite to hypoiodite; it is also favoured by high concentration, high temperature, and by the presence of other electrolytes.

The decomposition with liberation of free oxygen is also affected by the presence of free acid. Thus chlorinated solutions of aluminium or zinc hydroxides are more active bleaching agents than those of the alkalis or alkaline earths on account of their greater hydrolysis. For the same reason solutions of hypochlorite prepared electrolytically are more active than those made by passing chlorine into the alkaline solution, as they do not contain free alkali. If carbon dioxide is passed through an alkaline solution the bleaching power is also increased, as the free alkali is thus removed. A high concentration of hypochlorite is detrimental in bleaching, as the chlorate formed is inactive.

The bleaching action which is common to all hypochlorites is an oxidising action, and the oxidising action is also useful for other purposes. Thus when a hypochlorite or other hypohalogen salt is added to solutions of bivalent manganese, lead, nickel, cobalt or iron, the higher hydroxide is precipitated, and with manganese the reaction may even proceed as far as the formation of permanganate. Similarly, acids in a lower stage of oxidation are oxidised; e.g. phosphorous acid is converted into phosphoric acid by hypochlorites, and the

[1] *J. prakt. Chem.*, 1899 (ii.), 59, 53.

hydrides of the non-metals are rapidly attacked. The most remarkable reaction of this type is the liberation of free nitrogen from ammonia and compounds which contain the NH_2 group; *e.g.* urea. This is applied in the gas-volumetric determination of these compounds: $2NH_3 + 3NaBrO \longrightarrow N_2 + 3NaBr + 3H_2O$. In a similar way hydrogen peroxide is decomposed with liberation of free oxygen, $H_2O_2 + NaOCl \longrightarrow H_2O + O_2 + NaCl$, and even bromine and iodine are oxidised to bromate and iodate by the action of hypochlorite.

The oxidising power of the hypo-acids may be compared by using a hydrogen electrode as described on p. 164. The results for these substances given below indicate that the hypochlorite is the most powerful of the three agents:

$$Cl' + H_2O + 2 \oplus \longrightarrow H\cdot + HClO + 1\cdot49 \text{ volt.}$$
$$Br' + H_2O + 2 \oplus \longrightarrow H\cdot + HBrO + 1\cdot35 \quad,,$$
$$I' + H_2O + 2 \oplus \longrightarrow H\cdot + HIO + 1\cdot00 \quad,,$$
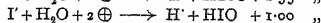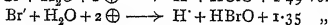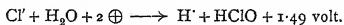
The *salts of the hypo-acids* are not known in the solid state, with the exception of the hypochlorites of sodium and calcium. The former is made by saturating a concentrated solution of sodium hydroxide with chlorine, with continual addition of more free alkali. The sodium chloride crystallises out first, and the hypochlorite is obtained from the mother liquor as fine needles with about 6 mols. of water of crystallisation. These crystals decompose easily when wet, but are stable if thoroughly dried. The calcium salt, $Ca(OCl)_2 . 4H_2O$, also forms fine needles, and in the dry state is more stable than bleaching powder. Anhydrous $Ca(ClO)_2$, mixed with a little free $Ca(OH)_2$ is sold as "perchloron," and although it contains about twice the available chlorine of commercial bleaching powder it is almost without smell.

Bleaching powder is a substance related to the hypochlorites, but its actual constitution is not fully elucidated. It is formed when slaked (but otherwise dry) lime is treated with gaseous chlorine, and is most active when prepared at somewhat above room temperature. A slight excess of water is unavoidable in the manufacture, and the product is a loose powder which is certainly not a mere mixture of chloride and hypochlorite, such as would be formed according to the equation $2Ca(OH)_2 + 2Cl_2 \longrightarrow CaCl_2$, aq. $+ Ca(OCl)_2$, which is analogous to the reaction of chlorine with caustic soda. It has, in fact, been demonstrated that an artificial mixture of the two salts has properties quite different from those of bleaching powder. The product always contains free CaO, which is probably unable to react with the chlorine when not slaked—addition of water makes it possible to produce a richer bleach (Ditz). The technical product may also be far from uniform, for heat is developed when different layers are mixed, owing to reaction between the different portions. The hypochlorite content can also be increased beyond that demanded by a reaction

producing equal numbers of molecules of chloride and hypochlorite. If an inert gas is passed over fresh bleaching powder, several per cent. of chlorine can be removed. This may be described as "adherent," but the quantity is sufficient to suggest chemical decomposition. The residue then contains 39 per cent. of chlorine.

The formula of Odling, $Ca\langle{}^{OCl}_{Cl}$ which is commonly used, fails to account for this or for the presence of free lime and water in the powder. It is likely that bleaching powder is not a single substance, but an equilibrium mixture containing not only this compound but lime and water as well. According to Neumann and Hauck,[1] a quarter of the lime is not chlorinated, so that bleaching powder may be a basic salt of formula $3CaOClCl, CaO, 4$ or $6H_2O$.

The material has recently been studied by the phase rule, the microscopic and the X-ray methods.[2] The initial stage in the preparation of bleaching powder is thus found to be the formation of basic hypochlorite, $Ca(OCl)_22Ca(OH)_2$ (I.) and basic chloride $CaCl_2Ca(OH)_2H_2O$ (II). By further chlorination, I is converted to a substance, apparently a mixed crystal, consisting mainly of $Ca(OCl)_2$. Ordinary bleaching powder consists of this mixed crystal and the basic chloride, II; this is a very stable substance which accounts for the non-deliquescent nature of bleaching powder, and for the difficulty of introducing more than about 35 per cent. of available chlorine.

The characteristic properties of bleaching powder depend on the presence of the hypochlorite radical; oxygen is given off in the presence of cobalt salts; the carbon dioxide of the air causes hydrolysis and in consequence a smell of hypochlorous acid, while on heating dehydration and the formation of chloride and chlorate take place. The last reaction occasionally takes place spontaneously with explosive violence. Bleaching powder, however, is of no use as an explosive; like pure calcium hypochlorite it is an oxygen carrier, and resembles saltpetre to some extent without being as effective, except that it reacts at lower temperatures.

Oxygen Fluorides.

Three oxygen fluorides have been prepared:[3] OF_2, O_2F_2 and OF. Fluorine is more electronegative than oxygen and formulae and nomenclature follow the usual practice of placing the more positive element first. Although OF_2 corresponds to Cl_2O in formula, it is not easily compared with it in manner of formation or properties.

[1] Z. Elektrochem., 1926, 32, 18.

[2] Bunn, Clark and Clifford, Proc. Roy. Soc., 1935, A 151, 141.

[3] Lebeau and Damiens, Compt. rend., 1927, 185, 652; 1928, 188, 1253; Ruff, Z. anorg. Chem., 1930, 190, 257; Ruff and Menzel, ibid., 1933, 211, 204.

It is similar in negative heat of formation (ca. 4·6 Cals.) but can be liquefied only at a temperature 150° lower than the chlorine monoxide, viz. at $-144\cdot8°$. Fluorine oxide is not very explosive and the dry gas is not detonated by electric sparks, though the presence of moisture causes decomposition of the gas under these conditions.

It is prepared by the electrolysis of moist fused KHF_2 below 100°, or better by passing fluorine into dilute sodium hydroxide solution: $2F_2 + 2NaOH \longrightarrow 2NaF + H_2O + OF_2$. No hypofluorite is formed, and on prolonged contact with the NaOH the following decomposition sets in: $OF_2 + 2NaOH \longrightarrow 2NaF + H_2O + O_2$. Dennis and Rochow,[1] by the interaction of fluorine and concentrated potassium hydroxide at $-20°$, obtained a relatively stable oxidising solution, which they consider contained hypofluorite or fluorite; they also prepared salts of the formula MFO_3.

This oxide of fluorine is an oxidising agent; both HCl and KI are attacked, with liberation of the halogen contained: $OF_2 + 4HI \longrightarrow 2I_2 + 2HF + H_2O$. Ammonia is oxidised, not merely to nitrogen, but partly to nitric acid. The gaseous OF_2 is colourless, but the liquid is a deep but slightly brownish yellow; it solidifies at $-223\cdot8°$. The smell is irritating, but different from that of fluorine.

O_2F_2 is formed as a yellow solid when a mixture of oxygen and fluorine at 15 mm. pressure is passed through a discharge tube cooled in liquid air. OF is possibly obtained as a colourless gas when the temperature of O_2F_2 is allowed to rise above $-100°$; O_2F_2 is not re-formed on cooling. Though the evidence for the existence of OF is weak, one might expect the molecule to be sufficiently stable to be isolated. It may be regarded as a resonance hybrid with a two-electron and a three-electron bond:

$$: O \text{----} \ddot{F} :$$

or more fully,

$$\{ : \ddot{O} \text{----} \ddot{F} : \, , \; : \ddot{O} \text{----} \ddot{F} : \}$$
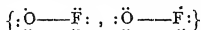
since O and F are somewhat similar in electronegativity.

Chlorates, Bromates and Iodates

These salts are more closely related to the hypo-salts than are the other oxy-halogen salts; indeed the hypo-salts can be regarded as an intermediate stage in the formation of the halogenates. The importance of the concentration of free acid on this transformation has been pointed out on p. 367, as also the greater ease of conversion of the hypiodites owing to their greater hydrolysis. This reaction, indeed, occurs even in presence of excess alkali, since even then there is enough free

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[1] *J. Amer. Chem. Soc.*, 1933, 55, 2431.

hypiodous acid present. The formation of bromate from hypobromite is not decreased in the presence of small quantities of alkali, but the change of hypochlorite to chlorate is almost completely inhibited by excess alkali. (Hence slaked lime is added to bleaching powder to make it more stable in hot climates.) In a solution of the same concentration in alkali the change in the hypobromite takes place 100 times, in the hypiodite 3,000,000 times as rapidly as in hypochlorite. Rise in temperature and the presence of other electrolytes also increase the rate of conversion.

This reaction is applied to the technical production of the halogenates, particularly of the chlorates. Electrolytic methods are now commonly employed; when a solution of potassium chloride is electrolysed without diaphragm, the Cl formed at the anode diffuses towards the cathode and reacts with the KOH formed at that pole, with production of hypochlorite. If the solution is strongly alkaline the hypochlorite is oxidised, but considerable evolution of free oxygen also occurs, representing a loss of energy. The hypochlorite is converted into chlorate in the way previously discussed; acidity of the solution increases the yield, but the liquid must not be too strongly acid or formation of hypochlorite is prevented by dearth of hydroxyl ions. Further, when the hypochlorite reaches the cathode it is reduced, but this can be prevented by adding to the solution substances which will form a layer over the pole and act as a diaphragm. Thus, calcium salts give a layer of calcium hydroxide over the cathode, but the addition of 0.2 per cent. potassium dichromate is still more effective,[1] as it forms a thin coating of chromium hydroxide over the cathode.

The electrolytic preparation of bromate and iodate can be carried out on the same lines, but here the presence of free acid is of no advantage. It is remarkable that while the hypochlorite ions are oxidised at the anode, hypobromite and hypiodite ions are not thus oxidised in neutral solution:

$$6ClO' + 3H_2O + 6\oplus \longrightarrow 2ClO_3' + 4Cl' + 6H^{\cdot} + 3O.$$
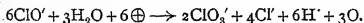
The Br' and I' ions keep the anode potential low. The secondary formation of halogenate, however, proceeds rapidly. The concentration of BrO' solutions formed electrolytically can thus be much higher than that of hypochlorite solutions. Naturally, the halogenate can be formed by addition of free halogen to alkali, and this method is used in the preparation of the relatively small quantities of bromate and iodate normally required.

Chlorine forms chlorates indirectly, with hypochlorite as an intermediate product, but iodine can be oxidised direct to iodate. When iodine is treated with fuming nitric acid, permanganate or neutral chromate solution, for example, iodates are formed. Even calcium

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[1] Müller, *Z. Elektrochem.*, 1899, **5**, 469.

hypochlorite converts iodine into iodate, and one might suspect that hypiodite is first formed; but this is a very improbable course for the reaction to take. Chlorates also form iodates with iodine, not by mere substitution, but according to the following equation, as free acid is formed:

$$5KClO_3 + 3I_2 + 3H_2O \longrightarrow 6HIO_3 + 5KCl.$$
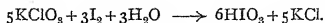
This is one of the most convenient ways of preparing iodic acid.

The formation of free bromic and iodic acids in the following equations is analogous:

$$5AgBrO_3 + 3Br_2 + 3H_2O \longrightarrow 5AgBr + 6HBrO_3,$$
$$5AgIO_3 + 3I_2 + 3H_2O \longrightarrow 5AgI + 6HIO_3.$$
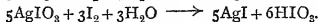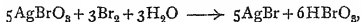
Iodine chloride is even more readily oxidised by chlorate than free iodine: $KClO_3 + ICl \longrightarrow KIO_3 + Cl_2$; chlorine is passed into a suspension of iodine in water and the requisite quantity of chlorate added. The oxidising action of chlorine on iodine must be borne in mind in detecting iodine by the addition of chlorine water; if an excess of chlorine is added, the chloroform solution of iodine is decolorised owing to the formation of iodate: $I_2 + 5Cl_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl.$

The behaviour of the bromates is intermediate, as may be expected. They can oxidise free iodine to iodate, but chlorine does not liberate bromine from them. Chlorates oxidise bromine to the bromate stage; so that, in general terms, chlorates are the most powerful, and iodates the least powerful of the three oxidising agents. Chlorine is not oxidised by iodates, but iodine is converted to iodate by chlorine. The relations can be expressed numerically by the oxidation potential of the halogenate ion compared with the free halogen, which shows a continuous increase from iodine to chlorine, thus:

$$I' + 3H_2O + 6\oplus \longrightarrow IO_3' + 6H^{\cdot} = 1 \cdot 08 \text{ volt.}$$
$$Br' + 3H_2O + 6\oplus \longrightarrow BrO_3' + 6H^{\cdot} = 1 \cdot 41 \quad ,,$$
$$Cl' + 3H_2O + 6\oplus \longrightarrow ClO_3' + 6H^{\cdot} = 1 \cdot 45 \quad ,,$$
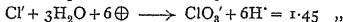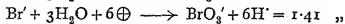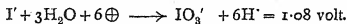
The continuity of the series does not hold for all reactions, and the iodates and iodic acid in particular show specific properties which probably point to a difference in constitution.[1] The heat of formation varies irregularly, as can be seen from the following values for the production of a molecule of the acids from halogen, oxygen and hydrogen in presence of water: chloric acid, 23·94 Cals., bromic acid, 12·42 Cals., iodic acid, 55·80 Cals. Bromic acid has the lowest heat of formation; this is probably due to the polymerisation of iodic acid, the heat of polymerisation being included in the heat of formation, while the other two acids are not polymerised. The complexity of the iodic

[1] A similar difference in the last member occurs in the series sulphuric, selenic and telluric acids.

acid molecule can also be detected by molecular weight determinations by the boiling point and freezing point methods, and is further indicated by the precipitation of albumin from solution by iodic acid—a reaction confined to acids of high molecular weight. The existence of numerous acid iodates is also not in conformity with the simple formula for iodic acid; typical acid iodates of univalent metals are $MH(IO_3)_2$ and $MH_2(IO_3)_3$. The polymerisation seems to be confined to acid solutions and is not shown by the neutral salts. It increases, moreover, with the concentration of the acid, and in general features the phenomenon is analogous to that previously described for hydrofluoric acid (p. 221).

Iodic acid may contain a hydrogen bond, (see p. 346), as does $(HF)_2$ *i.e.* F......H......F......H and $O_3I......H......IO_3......H$. If one of the H atoms is replaced by a metal the strength of attachment of the remaining H atom differs from that of the metal atom :

$$[HF_2]M \qquad\qquad [H(IO_3)_2]M.$$

The metal is linked ionically but the hydrogen atom is not dissociated from the acid radical. Nitric and metaphosphoric acids show similar effects. Iodic acid can form, besides these autocomplexes, double compounds with sulphuric, selenic, telluric, molybdic, phosphoric, tungstic and vanadic acids, which will be discussed in due course.

The stability of iodic acid compared with bromic and chloric acids also reflects its different constitution. It can be obtained anhydrous and on heating is converted into its anhydride. When, on the other hand, solutions of chloric and bromic acids are prepared by such methods as the decomposition of the potassium salts with hydrofluosilicic acid, or of the barium salts with sulphuric acid, they begin to decompose at quite moderate concentrations, giving off halogen and oxygen, chloric acid being partly converted into perchloric acid. The solutions of these two acids smell like nitric acid when not too dilute, whereas iodic acid is odourless. Chloric acid can be concentrated *in vacuo* at room temperature up to a strength corresponding to $HClO_3$, $4.5H_2O$ (52 per cent.), and bromic acid to $HBrO_3, 7H_2O$ (50.6 per cent.). Some decomposition occurs before this stage is reached, and attempts to concentrate further result in very rapid evolution of the decomposition products. The stability of these acids is much less at higher temperatures.

When a dilute solution of iodic acid is evaporated a viscous solution is obtained, containing about 70 per cent. of HIO_3 and showing a marked tendency to become supersaturated. The white crystals obtained from it are not deliquescent, and indeed effloresce at temperatures slightly above the ordinary, giving at 85° a pressure of aqueous vapour of 290 mm. They melt at 110° and pass reversibly into a mixture of solution and solid $3I_2O_5$, H_2O; this hydrate is stable up to 196°. At this temperature further dehydration

occurs, accompanied by remelting, thus: $3I_2O_5, H_2O \rightleftharpoons 3I_2O_5 + H_2O$. The anhydride, which forms a white powder, is remarkably stable. It melts with decomposition into iodine and oxygen at 300°. It dissolves easily in water, giving iodic acid, and owing to its stability it can be made in the dry way by oxidising iodine with chlorine dioxide and probably also with ozone. It is not attacked by Cl or Br, as can be readily understood from its production from iodine by oxidation with these elements. It oxidises carbon monoxide to carbon dioxide at moderate temperatures, a reaction which finds useful application in gas analysis.

Salts.—The normal salts of iodic acid do not differ much from the bromates and chlorates; they probably have a similar constitution. Salts of these acids containing tervalent metals are almost unknown; they are very soluble and probably have a high water content in the solid state. In contrast to these, the salts of the univalent metals are not hydrated, with the solitary exception of sodium iodate. The halogenates of bivalent metals have a moderate water content; the table below gives the number of molecules of water of crystallisation which they contain at room temperature:

	Ba	Ca	Mg	Ni	Co	Cu	Zn	Cd	Hg
Chlorate	1	2	6	6	6	6	6	2	2
Bromate	1	1	6	6	6	6	6	1	2
Iodate	1	6	4	4	4	1	2	1	0

The iodates generally are least hydrated and their solubility is also the least, while that of the chlorates is the greatest. Some iodates are only slightly soluble. Bin- and higher iodates $MH(IO_3)_2$, $MH_2(IO_3)_3$ are common; these types are not found in the chlorates and bromates. The following table gives a summary of the solubility of some of the most characteristic salts of this series:

SOLUBILITY IN G. ANHYDROUS SALT PER 100 G. WATER

	Rb	K	Na	Li	Hg^I	Ag	Ba
Chlorate	5 (20°)	7.2 (20°), 55.5 (100°)	99 (20°), 204 (100°)	313.5 (18°)	sol.	9 (20°)	37.0 (20°), 119 (100°)
Bromate		6.9 (20°), 49.8 (100°)	34.5 (20°), 90.9 (100°)	153.7 (18°)		0.16 (20°)	0.65 (20°)
Iodate	2 (20°)	8.1 (20°), 32.1 (100°)	9.1 (20°), 33.9 (100°)	80.3 (18°)	sl. sol.	0.044 (20°)	0.02 (20°), 0.2 (100°)

	Ca	Mg	Cd	Co	Hg^{II}
Chlorate	177.8 (18°)	128.6 (18°)	76.4 (18°)		
Bromate				0.15	
Iodate	0.26 (20°)	6.8 (20°)		0.83 (18°)	sl. sol.

On heating, the hydrated salts lose their water of crystallisation without further decomposition—a property confined to salts of the strongest acids. In fact, judging from their conductivity, these are

among the most highly ionised acids. The alkali salts melt without decomposition:

	NaClO$_3$	NaBrO$_3$	KClO$_3$	KBrO$_3$
Melting point	261°	384°	ca. 350°	370°

but decompose at a slightly higher temperature. The iodates are again the most stable, and, like the bromates, decompose with simple evolution of oxygen, giving the halide: $2KIO_3 \longrightarrow 2KI + 3O_2$; or else halogen is evolved with the oxygen and an oxide is left: $2M(BrO_3)_2 \longrightarrow 2MO + 2Br_2 + 5O_2$. Chlorates decompose similarly, but with the salts of the alkalis much perchlorate is produced: $4KClO_3 \longrightarrow KCl + 3KClO_4$. The chlorate is an intermediate stage of oxidation and decomposes into the higher and lower states.

Oxidising Action.—The evolution of oxygen from chlorates is an exothermic reaction and often takes place with explosive violence; the spontaneous explosion of potassium chlorate has been repeatedly observed. As a rule, however, the evolution of oxygen is retarded by the fact that the constitution of the form which evolves oxygen differs from that of the ordinary chlorate (see below). The addition of catalysts accelerates the decomposition, and manganese dioxide (pyrolusite), which is mostly used, causes a brisk evolution of oxygen at the melting point; this substance forms intermediate compounds (p. 173), but mere surface action, such as can be obtained by adding fine sand or powdered glass, also increases the rate at which oxygen is given off by the melt. The solid crystals decompose interfacially, starting from nuclei on the surface and spreading parallel to the crystal edges. At 223° the reaction is not catalysed by manganese dioxide in contact with the crystal.[1]

If the oxygen given off is employed in an exothermic oxidation the decomposition of the chlorate is greatly accelerated, and the mass usually explodes, *e.g.* when potassium chlorate is heated, or even merely rubbed with sulphur, phosphorus, charcoal, etc., the oxides of these substances being formed. Many organic compounds, *e.g.* sugar, are oxidised with similar vigour, and the reaction of chlorates with finely divided metals is also very energetic; excess of chlorate in contact with the explosive mixture also explodes at the same time. The oxidising action of bromates is less pronounced than that of the chlorates. Even the chlorates lose their oxidising efficiency in neutral or alkaline solution, but when acidified the property appears again. Hence it is clear that it is not compounds of formula I. which have the oxidising property, but the (pseudo) acids of formulae II. or III. (see p. 360):

$$
\text{I.} \quad \mathrm{ClO}\!\!\begin{Bmatrix} \mathrm{O} \\ \\ \mathrm{O} \end{Bmatrix}\!\!\mathrm{R.} \qquad \text{II.} \quad \left[\mathrm{Cl}\!\!\begin{array}{c} \mathrm{O_3} \\ \mathrm{R} \end{array} \right]. \qquad \text{III.} \quad \left[\mathrm{Cl}\!\!\begin{array}{c} \mathrm{O_2} \\ \mathrm{OR} \end{array} \right]
$$
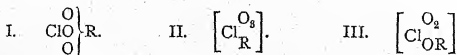
This explains the stability of the salts compared with the free acids,

[1] Coppock, Colvin and Hume, *Trans. Farad. Soc.*, 1931, 27, 283.

which readily decompose in the pure state. Even iodic acid acts as an oxidising agent in aqueous solution, and at a moderate temperature attacks silicon, carbon, sulphur and phosphorus, converting them into their highest oxy-acids; phosphorous and arsenious acids are oxidised, as are also hydroxylamine, hydrogen sulphide, etc., but all these actions proceed quietly. In contrast, free chloric acid oxidises with explosive violence when, for example, it is generated in the presence of organic matter: if filter paper is used in the preparation of the acid it is ignited, and even the diluted acid oxidises sulphur and phosphorus, converts iodine into iodic acid, and bleaches dyes.

The oxidation of the halogen hydracids by the oxyacids has been studied in most detail, e.g. $HClO_3 + 5HCl \longrightarrow 3Cl_2 + 3H_2O$; $HIO_3 + 5HI \longrightarrow 3I_2 + 3H_2O$. In acid solution these reactions go almost completely to the right, but in alkaline solution the reaction is largely reversed owing to the removal of the $H^{\cdot}$ ions, so that the salts of the oxyacids can be prepared by the action of the free halogen on alkaline solutions. In presence of HCl (at least $4N$) the following reaction proceeds quantitatively: $HIO_3 + 2HI + 3HCl \longrightarrow 3ICl + 3H_2O$ or if $N.HCN$ is used the action is $HIO_3 + 2HI + 3HCN \longrightarrow 3ICN + 3H_2O$ Both these reactions find useful application in volumetric analysis.

Applying the following expression for the equilibrium constant:

$$\frac{[Br']^5 \times [BrO_3'] \times [H^{\cdot}]^6}{[Br_2]^3} = K,$$

with similar equations for chlorine and iodine, the values of the hydrolysis constant K in acid solution are found to be:

Chlorine	Bromine	Iodine
10^{-5}	10^{-33}	10^{-47}.

The bromine reaction proceeds at a rate which is easily measured and is found to be quadrimolecular. It cannot therefore be kinetically as indicated in the equations given above, but one reaction between four components must proceed slowly, while other actions rapidly complete the transformation. The formation of bromous acid may be expected for other reasons, which makes the primary reaction as follows: $2H^{\cdot} + Br' + BrO_3' \longrightarrow HBrO + HBrO_2$. The bromous and hypobromous acids are then reduced at a very rapid rate by more hydrobromic acid, thus:

$$H^{\cdot} + Br' + HBrO \longrightarrow H_2O + Br_2,$$
$$3H^{\cdot} + 3Br' + HBrO_2 \longrightarrow 2H_2O + 2Br_2,$$
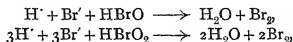
giving bromine as the final product. If hydriodic acid is used in place of hydrobromic acid the reaction goes forty-five times as fast; the addition of acids and of certain salts[1] also accelerates the reaction, though some salts act as negative catalysts (e.g. $CdBr_2$). Similar

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[1] Schilow, Z. physikal. Chem., 1898, 27, 513.

relations for the chlorine acids have been obtained by Foerster and Dotch.[1]

Some of the oxidising actions of bromic acid require to be induced by addition of a reducing agent. Thus the pure acid is not reduced by arsenious acid, but if a little sulphur dioxide or ferrous salt is added the reaction starts and proceeds to the end, long after the whole of the inductor is used up. As hydrobromic acid acts as an inductor the reaction is self-inducting, and once it has begun it proceeds with increasing speed. Iodic acid behaves in a similar way.

The halogenate acids are weaker oxidising agents than the hypo-halogen acids, although they contain more oxygen. The oxidising power can be valued by the determination of the electrical potential; the following results are obtained in acid solution at $20°$:

$$0^{\epsilon}_{Cl_2 \dashrightarrow HClO} \approx 1\cdot59 \text{ volt.} \qquad 0^{\epsilon}_{Br_2 \dashrightarrow HBrO} \approx 1\cdot59 \text{ volt.}$$
$$0^{\epsilon}_{Cl_2 \dashrightarrow ClO_3'} = \text{ca. } 1\cdot45 \text{ volt.} \qquad 0^{\epsilon}_{Br_2 \dashrightarrow BrO_3'} \approx 1\cdot49 \text{ volt.}$$
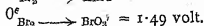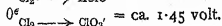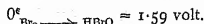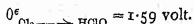
This somewhat unexpected result is quite a general phenomenon, as has been shown by Luther[2]; when compounds intermediate in state of oxidation decompose spontaneously into a higher and a lower state, they are more powerful oxidising agents than the higher compound and more powerful reducing agents than the lower compound. The following reactions are examples of decompositions of this type:

$$Cu^{\cdot} \longrightarrow Cu^{\cdot\cdot} + Cu \qquad 2HgI \longrightarrow HgI_2 + Hg \qquad HClO \longrightarrow HClO_3 + HCl$$
$$Sn^{\cdot\cdot} \longrightarrow Sn^{\cdot\cdot\cdot\cdot} + Sn \qquad HNO_2 \longrightarrow NO + HNO_3 \qquad HClO_3 \longrightarrow HClO_4 + HCl$$
$$AuCl \longrightarrow AuCl_3 + Au \qquad H_2MnO_4 \longrightarrow HMnO_4 + MnO_2.$$
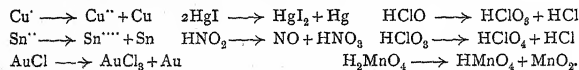
Thus, for example, on oxidising metallic copper, a stronger reducing agent $(Cu^{\cdot})$ is produced, while when cupric ions are reduced the cuprous ions are more powerful oxidising agents than the former. Similarly, hypochlorites, which decompose spontaneously into chlorides and chlorates, are stronger oxidising agents than the chlorates.

Chlorine Dioxide and Chlorous Acid

Chloric and iodic acids behave differently in contact with concentrated sulphuric acid; chloric acid decomposes into perchloric acid and chlorine dioxide. This reaction occurs in two stages. First, the spontaneous decomposition of the chloric acid gives chlorous and perchloric acids, $2HClO_3 = HClO_2 + HClO_4$, and then the chlorous acid reacts with the unchanged chloric acid: $HClO_2 + HClO_3 = 2ClO_2 + H_2O$.

It is dangerous to attempt to prepare any quantity of chlorine dioxide by this method, as the compound readily explodes, particularly in presence of easily oxidisable substances like sulphur, phosphorus, and any kind of organic matter such as cork, rubber, sugar, etc. The

[1] Z. Elektrochem., 1917, 23, 137.
[2] Z. physikal. Chem., 1901, 36, 385.

preparation is free from danger if the chlorate is acted on by moist oxalic acid: $2HClO_3 + H_2C_2O_4 = 2ClO_2 + 2H_2O + 2CO_2$. The gas is evolved in a regular stream when the mixture is heated to 60°, and can easily be freed from the carbon dioxide which accompanies it by liquefying the chlorine dioxide. At 10° it forms a dark brown liquid of about the same colour as bromine, and freezes at −76° to orange crystals. In the gaseous state the compound is intensely yellow, and many of its physical properties lie between those of chlorine and bromine (e.g. melting point, boiling point, density). When pure it does not explode below 100°, and it can be kept for a long time in the dark without decomposition; it is slowly decomposed on exposure to light.

The molecular weight of chlorine dioxide corresponds to the formula ClO_2, and has been determined by the freezing and boiling points of solutions of the gas in carbon tetrachloride. It is readily soluble in concentrated sulphuric acid at −18°, but is largely decomposed when expelled by warming. From an aqueous solution it can be expelled without decomposition, and it is scarcely hydrolysed at all into chlorous and chloric acids. The saturated solution contains 20 vols. of the gas at 0°, is deep yellow in colour, and gives a hydrate analogous to those of chlorine and bromine. It is probably an octahydrate and decomposes into water and ClO_2 at 18·2°.

It might be supposed that the acids formed on hydrolysis in aqueous solution would react to reproduce water and chlorine dioxide, $HClO_2 + HClO_3 \longrightarrow 2ClO_2 + H_2O$, but experiments on the distribution of the gas between water and carbon tetrachloride have shown that the gas exists as such in the water. The relative distribution is constant and independent of the concentration. As the ClO_2 is dissolved unchanged in CCl_4, the ratio would not be constant if it was hydrolysed in aqueous solution. Further, silver nitrate gives a precipitate of the slightly soluble chlorite after a long time only; and conversely, solutions of chlorites remain colourless for some time after acid is added, and only slowly acquire a yellow colour. Attempts to prepare the anhydride, Cl_2O_3, have been unsuccessful, but the egg-yellow solid BrO_2 has been isolated.[1]

When hydroxyl ions are present the hydrolysis of chlorine dioxide proceeds with much greater rapidity, and with sodium hydroxide chlorate and chlorite are formed after a short time: $2ClO_2 + 2NaOH \longrightarrow NaClO_3 + NaClO_2 + H_2O$. This reaction is analogous to the formation of nitrate and nitrite from nitrogen dioxide (p. 674). It does not always take place rapidly, and if the concentration of hydroxyl ions is low, as, for example, in solutions of bicarbonate, it may take some weeks to go to completion at 0° in the dark.[2]

An equivalent quantity of chlorate is always produced when chlorites

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[1] Schwartz and Schmeisser, Ber. 1937, 70, 1163.

[2] Bray, Z. physikal. Chem., 54, 731 ; Z. anorg. Chem., 1906, 48, 217.

are formed by the hydrolysis of the dioxide; the chlorite can be obtained free from chlorate if a peroxide is used in the decomposition :
$$2ClO_2 + Na_2O_2 = 2NaClO_2 + O_2.$$

Chlorous acid, like hypochlorous and chloric acids, is a strong oxidising agent in the free state, but not in the form of salts. This property may again be due to a difference in structure, and it is likely that only the undissociated acid acts as an oxidiser. It is not highly dissociated in solution, and is intermediate in strength between hypochlorous acid and chloric acid; it is, however, stronger than carbonic acid and is scarcely liberated from its salts by a current of CO_2.

The salts are in general yellowish in colour and easily soluble. Those of the alkalis are even deliquescent, but the yellow lead, silver and mercurous salts, together with the red mercuric chlorite, are insoluble. The chlorites of the other heavy metals can be prepared by the double decomposition of the sulphates with barium chlorite, after the addition of alcohol. There are characteristic double salts containing alkali chlorites and copper chloride. Some of the chlorites of the noble metals explode when struck or heated. All the chlorites are crystalline, those of the alkalis and those which are slightly soluble being anhydrous; those of Zn, Cd and Ni contain 2 mols. of water of crystallisation.[1]

The iodine compounds corresponding to ClO_2 and $HClO_2$ do not exist. Bromous acid is assumed as an intermediate stage in many reductions, but it has not been isolated. IO_2 is not analogous to ClO_2 but is probably a basic iodate—$O : I . IO_3$.

Perchloric Acid

The very fragmentary similarities between the oxy-halogen compounds become still less marked in the higher acids; it is therefore preferable to discuss them separately.

Concentrated solutions of chloric acid decompose spontaneously in the cold and more rapidly on heating, with formation of perchloric acid and lower oxides of chlorine. In a similar way, chlorates give perchlorates as well as chlorides when heated to the point at which oxygen is evolved. It follows from Luther's Rule (p. 376) that perchlorates will be less powerful oxidising agents than chlorates; this has been confirmed by measurements of electrical potential, and agrees with the greater stability of perchloric acid and its salts. Perchloric acid can even be isolated and kept in the pure state. Its anhydride is also stable, and distils as a colourless oily liquid when the acid is warmed with phosphorus pentoxide; the Cl_2O_7 decomposes slowly on keeping, but explodes on percussion. When water is added the anhydride is rehydrated to the acid.[2]

[1] *Cf.* G. R. Levi, *Gazetta*, 1923, 53 (i), 105, 200, 245.
[2] Michael and Conn, *Amer. Chem. J.*, 1900, 23, 10.

The perchloric acid which has the composition $HClO_4$ is not, however, a simple substance, but an equilibrium mixture of the acid with small quantities of Cl_2O_7 and water, which forms a hydrate with the perchloric acid. The presence of the anhydride is shown by the alteration in boiling point of the acid. It begins to boil at $39°$ under a pressure of 56 mm., but the vapour is richer in anhydride than is required by the formula $HClO_4$, and contains 57 per cent. of Cl_2O_7 molecules instead of the 50 per cent. required for the pure acid. The residual acid thus becomes weaker in anhydride, *i.e.* more dilute, and the boiling point rises. The free anhydride contained in the acid is the cause of its slight lack of stability, for it gradually decomposes into chlorine dioxide and oxygen. The oxygen escapes and the ClO_2 remains in the liquid and gives it a dark-brown colour. When this slow decomposition has proceeded for some time there is a likelihood of explosion, and this has been observed in old anhydrous samples of $HClO_4$. The pure acid decomposes on heating to $92°$ as the Cl_2O_7 reverts into ClO_2 and oxygen, and fresh quantities are formed from the acid to maintain the equilibrium. The water forms hydrates with the perchloric acid. The acid is much less susceptible to reduction when hydrated, and whereas the pure acid explodes violently in contact with charcoal, paper, ether, etc., the diluted acid is proof against reduction by hydrogen sulphide, sulphurous and nitrous acids, indigo and even hydriodic acid. It is, however, reduced by ferrous and titanous salts, and by hyposulphites. The hydrates are also much more resistant to the action of heat. On distilling a weak solution, pure water comes off first until the boiling point has risen to $203°$, when an acid of composition $HClO_4 . 2H_2O$ passes over at constant temperature. Conversely, when an acid containing but little water is distilled, the pure acid distils over first, and the water accumulates in the less volatile portion until the same hydrate is formed. Six hydrates have been detected [1] with water content from 1 to 3.5 molecules; those which contain most water have the lowest freezing points. There are, however, well-defined eutectics between the maximum freezing points. The monohydrate freezes at $50°$ (it is really hydroxonium perchlorate, p. 381), and that with 3.5 molecules H_2O freezes at $-41.4°$. The pure acid is a mobile, colourless liquid at ordinary temperatures and freezes at $-112°$. It fumes in the air (probably owing to the Cl_2O_7 present), boils at $110°$ under 18 mm. pressure, and its density at $20°$ is 1.77. Heat is evolved on solution in water owing to the formation of hydrates. The monohydrate has some extreme properties; its density is greater than that of any other solution of the acid (1.8 at $50°$), and the viscosity also shows a maximum value. Perchloric acid is one of the strongest acids.

The aqueous solution is most readily prepared by treating a

[1] Wyk, *Z. anorg. Chem.*, 1905, 48, 1.

concentrated solution of the sodium salt with gaseous hydrogen chloride. Sodium chloride is precipitated, and the excess of HCl can be removed by heating the liquid.

In the preparation of the pure acid the properties outlined above must be taken into consideration. The distillation of aqueous acids made by such methods as the decomposition of the potassium salt with hydrofluosilicic acid, of the barium salt with sulphuric acid, or of the silver salt with hydrochloric acid, gives at most the dihydrate. But if the solid potassium salt is distilled with concentrated sulphuric acid under reduced pressure the acid is so slightly decomposed that at 160° a distillate of almost pure acid is obtained.[1]

Chlorine Heptoxide, Cl_2O_7.—When perchloric acid is allowed to stand after mixing it with P_2O_5, the colourless, liquid anhydride is formed (m.pt. : $-91.5°$; b.pt. : $82°$). This substance is but slowly rehydrated by water. It is more stable than the other oxides of chlorine and does not explode in contact with organic substances, though explosion takes place on percussion or ignition.

Perchlorates.—The alkali salts of perchloric acid are formed when the chlorates are heated (p. 374): $4KClO_3 \longrightarrow KCl + 3KClO_4$. The potassium salt is most easily isolated from the accompanying chloride, owing to its low solubility in water. As the chlorate decomposes into chloride and oxygen directly at the same time, this method of preparation is of no great practical value. Anodic oxidation is more efficient, and when chlorides are electrolysed in weakly acid solution, chlorates are first formed and then perchlorates ; a higher temperature favours the production of chlorate, while in the cold, with high E.M.F. and high current density, the perchlorate is more readily formed.

The general properties of the perchlorates depend to a large extent on the great volume and symmetrical structure of the perchlorate ion. The salts of such ions with small cations have a great tendency to form complexes so as to surround the small cation with other groups and preserve a spatial balance. The perchlorates of metals of small atomic volume are difficult to crystallise from aqueous solution, as they take up water molecules to a large extent and thus become similar to water in properties and miscible with it. Their great solubility has rendered it difficult to study them. When they are combined with groups other than water, these groups are held so tenaciously that it is difficult to replace them by water, and in consequence these complexes are only slightly soluble. Nickel hexammine perchlorate, $[Ni(NH_3)_6](ClO_4)_2$, is so insoluble that it can be used for the quantitative determination of nickel, and ammonia is only evolved from it with great difficulty ; on the other hand, magnesium and barium perchlorates can be used as dehydrating agents. In general, the more soluble the

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[1] Vorländer and Schilling, *Ann.*, 1900, **310**, 369.

hydrate the less soluble the ammine. When, however, the metal in the perchlorate is one of large atomic volume the properties are very different and neither ammines nor hydrates are formed. As the solubility of salts in water is largely dependent on hydration of the salt (though the definite formation of hydrates which can be isolated is not a necessary consequence of this), the perchlorates of bases of large volume are not very soluble. This effect is shown in the perchlorates of the more bulky metals (K, Rb, Cs), but when the size of the cation is increased by complex formation, as in the cobaltammines and the chromammines, the perchlorates become practically insoluble. These bases can thus be precipitated as perchlorates, although their basic properties are weak. In particular, many organic bases of almost negligible basic strength give insoluble perchlorates (*e.g.* carbinols, ketones, etc.). These have been investigated by Hofmann and his collaborators.[1] Perchloric acid can make use of the slightest basic tendencies to form salts. Even the very weak base hydroxonium hydroxide, $OH_3 \cdot OH$, the hydrate of water, can form a salt with perchloric acid—hydroxonium perchlorate, $OH_3 \cdot ClO_4$ (*i.e.* $HClO_4 \cdot H_2O$). An examination of the crystal structure of this compound shows[2] that it is a true salt and not a mere hydrate, for its structure is analogous to that of ammonium perchlorate, NH_4ClO_4. Similarly, nitronium diperchlorate $[(HO)_3N](ClO_4)_2$ and monoperchlorate $[(HO)_2NO]ClO_4$ have been prepared.

The potassium salt is the best known of the perchlorates. It is anhydrous, and the solubility at 0° is 0·71 g., and at 100°, 18·7 g. in 100 g. of water, the solubility in alcohol being much less. It is used for the quantitative determination of potassium. The rubidium salt is even less soluble than potassium perchlorate, but the caesium salt is fairly soluble. The solubilities of the perchlorates of the alkaline earth metals, again, do not vary regularly with the atomic weight, the strontium salt being the most soluble. Other common perchlorates are: $NaClO_4 \cdot H_2O$, $LiClO_4 \cdot 3H_2O$, $AgClO_4$.

Almost all the perchlorates of the heavy metals are deliquescent; $Mg(ClO_4)_2$ is as efficient a dehydrating agent as P_2O_5. It is prepared by heating $Mg(ClO_4)_2 6H_2O$ at 200° or by heating at the same temperature and at 1-10 mm. pressure a mixture of ammonium perchlorate and magnesium carbonate. $Ba(ClO_4)_2$, similarly prepared from the trihydrate, is about as effective as H_2SO_4 as a drying agent, for which purpose mixtures of $Ba(ClO_4)_2$ and $Mg(ClO_4)_2$ have also been used.[3] Lead perchlorate is soluble in organic solvents and silver perchlorate dissolves readily in toluene.

[1] *Ber.*, 1910, 43; 1911, 44; *Ann.*, 1912, 386, 304.

[2] Volmer, *Ann.*, 1924, 440, 200.

[3] Smith and Hardy, *Z. anorg. Chem.*, 1935, 223, 1, 738, 930; Smith, *Ind. Eng. Chem.*, 1927, 19, 411.

The perchlorates are isomorphous with the permanganates, owing to the similarity in the structure of the radicals $[ClO_4]$ and $[MnO_4]$. They are stable to heat and decompose at a much higher temperature than the chlorates; they also explode when heated with carbon, but again not so readily as the chlorates.

Periodic Acid

The periodates are very different from the perchlorates; on heating they are decomposed into iodates and oxygen, and are therefore not formed, or only to a slight extent, when iodates are heated. It has been stated that they are produced when iodates of the alkaline earths are heated, but much oxygen and some free iodine are liberated at the same time.

In the chlorine series the lower oxyacids are better oxidising agents than those which contain more oxygen, but here the periodate oxidises more readily than the iodate, both as solid and in solution. Measurements of the oxidation potential give the sequence $IO' \longrightarrow IO_4' \longrightarrow IO_3'$ in decreasing oxidising power. Iodates can therefore be made from periodate and iodide, thus: $3IO_4' + I' = 4IO_3'$, though perchlorates do not undergo a similar reduction; naturally, if excess of iodide is present the iodate is further reduced to iodine.

The oxidising power of periodates is demonstrated by the fact that they develop ozone in solution at the ordinary temperature, with formation of iodate. This indicates that unlike perchloric acid, periodic acid is a true per-acid, so that the structure of the two acids cannot be comparable. Also, it is a weaker acid than iodic acid (whereas perchloric is stronger than chloric), and the ammines of its salts with small cations are more soluble than those of the perchlorates. If the constitutions of the two acids were similar, the periodates would have the greater volume, since the atomic volume of iodine is greater than that of chlorine. The complete absence of a perbromic acid would be difficult to understand if the two acids had the same structure.

Pauling[1] considered the magnitude of the co-ordination number of the central positively charged atom when surrounded by O, OH and OH_2 groups. Regarding the groups as rigid spheres, if the ratio (ρ) of the radius of the central atom to that of each of the surrounding groups is less than 0.225, three such groups completely occupy the available space (planar arrangement) and prevent the close approach or attachment of a fourth group. For $\rho = 0.225$ to 0.414 a tetrahedral arrangement is the stable form; for $\rho = 0.414$ to 0.713 an octahedral, and if ρ is greater than 0.713 a cubic structure is the stable variety.

[1] *J. Amer. Chem. Soc.*, 1933, **55**, 1895.

The following table shows the ratio of the radii of univalent cations and oxygen:

RO_3 Type .	.	Be^{2+}	C^{4+}	N^{5+}	
		0·20	0·17	0·14	
RO_4 Type .	.	Al^{3+}	Si^{4+}	P^{5+}	S^{6+}	Cl^{7+}
		0·41	0·37	0·34	0·31	0·28
				As^{5+}	Se^{6+}	Br^{7+}
				0·40	0·37	0·35
RO_6 Type .	.	Ga^{3+}	Ge^{4+}		
		0·46	0·43		
		In^{3+}	Sn^{4+}	Sb^{5+}	Te^{6+}	I^{7+}
		0·59	0·55	0·51	0·47	0·44

These results agree with the existence of the known compounds H_3BO_3, H_2CO_3, HNO_3. Crystal structure of metaborates (HBO_2), H_2SiO_3 and HPO_3 show that these are polymerised. The first is planar with three oxygens surrounding each boron, the others are tetrahedral with four oxygen atoms about each Si or P atom. Aluminium, a border-line case, gives both 4- and 6-types, as shown by the crystal structure of mica and sodalite; iodine also is not far into the RO_6 zone, which would account for the two types $H[IO_4]$ and $H_5[IO_6]$; chlorine and bromine both fall definitely within the RO_4 zone but it does not account for the non-existence of a perbromic acid.

The salts of periodic acid are very different from those of perchloric acid. The latter is invariably monobasic, while periodic acid is frequently polybasic—occasionally pentabasic. In the free state, however, it acts as a monobasic acid, for conductivity measurements have shown that there are only two ions per molecule in solution. The various hydrates may therefore be co-ordination compounds of water with the acid and not true polybasic acids. A dihydrate of formula $HIO_4 \cdot 2H_2O$ can be isolated, but not a monohydrate, though the free acid HIO_4 exists. In the presence of bases, however, the ions IO_6'''' and IO_5''' are stable in aqueous solution, and they probably also occur in small quantity in solutions of the free acid. When periodates are precipitated with silver salts the periodate Ag_5IO_6 is invariably obtained and the same salt is obtained by the action of water on other silver periodates. It is notably more insoluble than other silver periodates, and thus always tends to be formed in aqueous solution with exhaustion of that particular type of ion.

The following types of periodates can be obtained in the solid state:

M_5IO_6	M_3IO_5	$M_4I_2O_9$	MIO_4
i.e. $5M_2O$, I_2O_7	$3M_2O$, I_2O_7	$2M_2O$, I_2O_7	M_2O, I_2O_7
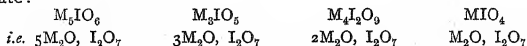
in which M is a univalent metal. There are also many salts of the complex acids in which only part of the hydrogen is replaced by the metal, *e.g.* $Na_2H_3IO_6$ and $Na_3H_2IO_6$, but the free acid is split off in

solution. The hydrogen of the hydrates of the acid which exist in solution is replaceable by metals, and the particular salt obtained from the solution depends entirely on the relative solubility of the possible products. It is not possible to predict what type of salt will be formed from a given solution as in the phosphates, where the ortho, meta and pyro states of hydration are stable in solution; but similar effects are observed in the arsenates and borates.

All the périodates are slightly soluble in water; thus the solubility in 100 g. of water is 0.66 g. KIO_4, 0.65 g. $RbIO_4$ and 2.15 g. $CsIO_4$, and the salts of the alkaline earth and heavy metals are for the most part still less soluble. The periodates are all heavy crystalline powders; many have water of crystallisation. They are distinctly more soluble in hot water, and addition of acids, particularly of nitric or periodic acids, still further increases their solubility. The colour of the salts is mostly that of their metal ions, but the less acid silver salts are black to brown, while the more acid ones are orange or yellow. Periodates decompose at high temperatures into iodate and oxygen and then into iodide or oxide; those of strong bases can be fused without much decomposition. Hydrogen sulphide or sulphur dioxide reduce the periodates in solution, and if these reagents are added in excess the iodide is formed direct without separation of free iodine; but otherwise the iodate and iodide formed by reduction react with liberation of iodine. The periodates, like the permanganates, are reduced by hydrogen peroxide with liberation of oxygen. The formation of complex acids with molybdic and tungstic acids will be mentioned later (p. 500 *et seq.*).

The periodates can be prepared by the oxidation of the iodates, either by chlorine, $NaIO_3 + 3NaOH + Cl_2 \longrightarrow 2NaCl + Na_2H_3IO_6$, or at the anode, using a diaphragm, or in presence of chromate with an anode of lead dioxide. The IO_4' ions are produced in either acid or alkaline solution, but a low temperature and (unlike the condition for perchlorate) a low current density are desirable. These salts are also formed when iodides are fused with sodium peroxide, or when free iodine is heated with barium peroxide.

The free acid is obtained by the decomposition of the barium salt with sulphuric acid or of the silver salt with hydrochloric acid. On evaporation, the hydrate H_5IO_6 is obtained in colourless deliquescent crystals, which melt at 134° with slight decomposition, but which are dehydrated to HIO_4 at 100° *in vacuo*; at 80° *in vacuo*, $H_4I_2O_9$ is obtained.[1] The anhydrous acid is very hygroscopic and hisses when added to water. It can be sublimed in a vacuum, but decomposes on heating in the open, giving I_2O_5 and oxygen.

Chlorine Hexoxide.—This compound can be regarded as the mixed anhydride of chloric and perchloric acids (see p. 358). It has been known for the last eighty years, but was always supposed to be a

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[1] Partington and Bahl, *J. Chem. Soc.*, 1934, 1088.

mixture. It has recently been shown to be a definite substance,[1] and is formed by the action of light or ozone on chlorine dioxide as a red oil, freezing at 3.5°, appearing black in thick layers. It can readily be distinguished from the other oxides of chlorine, from the element itself, and from oxygen, by its low vapour pressure (1 mm. at 20°). ClO_3 molecules are probably present in the gas, but the liquid contains[2] Cl_2O_6. This oxide is also produced when ozone acts on chlorine in red light but not in blue; and as red light is not absorbed by Cl, it follows that the light first acts on the ozone and then the more energetic product attacks the chlorine.

When mixed with other oxides of chlorine the hexoxide is very explosive—much less when it is pure. It explodes when mixed with organic substances. At the ordinary temperature it decomposes slowly into chlorine dioxide, oxygen and chlorine.

Chlorine Tetroxide, Iodine Tetroxide, Tribromine Octoxide.

When iodine is allowed to react with an ethereal solution of silver perchlorate the silver is removed and a stable solution containing ClO_4 or more probably its polymer $(ClO_4)_2$ is obtained. It reacts with metals like the free radical ClO_4, giving perchlorates, *e.g.* $Zn + (ClO_4)_2 \longrightarrow Zn(ClO_4)_2$; when the metal shows variable valency, the lower valent form is obtained, and copper, for instance, gives white $CuClO_4$. The solution of the ClO_4 must be kept more dilute than $N/10$ or the solvent is attacked.

The chlorine tetroxide (or its polymer) is colourless and not volatile in ether vapour. It is readily hydrolysed by water, thus: $(ClO_4)_2 + H_2O \longrightarrow HClO_4 + HClO_5$; but the acid $HClO_5$ is not obtained unless the silver salt is formed at once, by using Ag_2O in place of water for the decomposition. The tetroxide liberates iodine from iodides, but not in the calculated quantity. With free iodine an equilibrium is set up: $ClO_4 + I \rightleftharpoons Cl + IO_4$. The iodine tetroxide can be made in the same way as the chlorine compound, but it is easily decomposed.[3]

Tribromine Octoxide $(Br_3O_8)_n$.—This compound lies outside the main series of halogen oxides and its constitution is not yet known with any certainty. It is possible that it is not a true oxide but only a peroxide or ozonide. It is formed by treating bromine vapour with ozone at temperatures round about 0° and under diminished pressure. The oxide is deposited as a white coating on the walls of the reaction vessel, and has two crystalline forms, with a transition temperature of about −35°. At −80° it is stable for a day; it dissolves in water to an acid solution which liberates iodine from KI but does not contain free bromine.[4]

Basic Compounds of Iodine

Iodine is the only one of the halogen elements to form compounds in which it is definitely tervalent. These compounds can be prepared by the direct oxidation of iodine with ozone, nitric acid or sulphuric

[1] M. Bodenstein, P. Harteck and E. Padelt, *Z. anorg. Chem.*, 1925, 147, 233.

[2] Schumacher and Stieger, *Z. anorg. Chem.*, 1929, 184, 272; Goodeve and Richardson, *J. Chem. Soc.*, 1937, 294.

[3] Gomberg, *J. Amer. Chem. Soc.*, 1923, 45, 398.

[4] Lewis and Schumacher, *Z. Elektrochem.*, 1929, 35, 648; *Z. anorg. Chem.*, 1929, 182, 182.

acid. The iodine has a basic function in these compounds, and the salts formed with acids are derived from the hydroxide $I(OH)_3$. The behaviour of the iodine chlorides on electrolysis indicates that iodine can form positive ions as is also shown by the electrolysis of the acetate solution.[1] The organic substituted iodine compounds of the iodonium series are quite strong bases.

The action of ozone on solid or dissolved iodine gives the compound $I(IO_3)_3$, which Fichter and Rohner[2] consider to be an iodate of iodine. It is a yellowish white amorphous powder which is very hygroscopic, with formation of a black liquid from which iodic acid crystallises on long standing. The powder evolves iodine slowly at 75° and decomposes rapidly at 120°—hydrolysis gives rise to $I(OH)_3$ and HIO_3 in the usual way, and iodine is formed when these compounds interact. The phosphate, IPO_4, is formed by the oxidation of a mixture of iodine, phosphoric acid and acetic anhydride by fuming nitric acid, while heating iodic acid in phosphoric acid gives only iodine iodate. Iodine nitrate, analogous to the iodate, apparently exists, and iodine trichloride ICl_3 is the corresponding chloride. Fichter has prepared a series of organic iodosalts, IX_3, such as the acetate and its derivatives.

In conformity with the weakly basic properties of iodine, basic salts are more stable than the normal ones. When I_2O_5 is dissolved in sulphuric acid and the liquid warmed till iodine is evolved, a solution is obtained which slowly deposits yellow crystals usually formulated[3] as I_2O_3, SO_3, but Bahl and Partington[4] have shown it to be a mixture of $I_2O_3 . H_2SO_4$ and $I_2O_4 . H_2SO_4$. It is also obtained[5] by the interaction of iodine and I_2O_5 in the presence of sulphuric acid.

$$2I_2 + 3I_2O_5 \rightleftharpoons 5I_2O_3$$
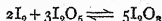
When other methods are employed other basic salts are obtained, with varying content of SO_3 and I_2O_4.[6] The oxide I_2O_4, which is regarded as the basic iodate, thus: $O : I . (IO_3)$, is obtained on hydrolysis of the basic sulphates. It also is a yellow powder, not hygroscopic nor soluble in water, though it dissolves in sulphuric acid. On boiling it with water it is hydrolysed in the same way as $I(IO_3)_3$, with formation of iodic acid, and it decomposes in the dry state when heated : $5I_2O_4 \longrightarrow 4I_2O_5 + I_2$. It cannot, however, be formed by partial hydrolysis of the normal iodate, and its formation when iodine is rubbed with nitric acid is another fact difficult to reconcile with its supposed basic character.

[1] Fichter and Stern, *Helv. Chim. Acta*, 1928, **11**, 1256.

[2] *Ber.*, 1909, **42**, 4093.

[3] Masson, *Chem. and Ind.*, 1937, **56**, 1034 ; *J. Chem. Soc.* 1938, 1702.

[4] *J. Chem. Soc.*, 1935, 1258

[5] Fichter and Kappeler, *Z. anorg. Chem.*, 1915, **91**, 134 ; Masson, Race and Pounder, *J. Chem. Soc.*, 1935, 1669.

[6] Kappeler, *Ber.*, 1911, **44**, 3501.

Compounds of the Halogens with one another

The following table gives the melting and boiling points of the known compounds of the halogens with one another; no known compound contains more than two different halogens.

		IF_5	IF_7	ICl_3	ICl	IBr
Boiling point	.	97°	5·6°	?	97·4°	116°
Melting point	.	−8°	4·5°	101° (16 atm.)	27·2° (α)	36°
					13·9° (β)	

		BrF	BrF_3	BrF_5	$BrCl$	ClF	ClF_3
Boiling point	.	20°	127°	40·5°	+5°	−100°	13°
Melting point	.	−33°	8·8°	−61·3°	−66°	−156°	−83°

In those compounds which contain more than two atoms the more electropositive (and larger) halogen can be regarded as the central atom surrounded by the smaller halogen atoms; the compound can be formed only when there is a sufficient contrast between these properties in the two halogens. Thus F cannot function as the central atom, but iodine can be surrounded with a number of atoms.

These compounds are formed when the free halogens are mixed either as gases or in any other state of aggregation, or in solution. The chlorine fluorides are formed [1] when the elements are heated together or fired with an electric spark, when there is a slight explosion. With iodine chlorides and fluorides where there are two compounds, the relative quantities present determine which is formed. The iodine chlorides can also be formed by oxidising an iodide with chlorine: $HI + 2Cl_2 \longrightarrow HCl + ICl_3$ or $HI + Cl_2 \longrightarrow HCl + ICl$. Alternatively, an iodate may be reduced with hydrochloric acid, giving free chlorine and iodine, which then combine and the following reaction is also useful (p. 375): $HIO_3 + 2HI + 3HCl \longrightarrow 3ICl + 3H_2O$.

The affinity of the halogens for each other is but slight, and thus the heat of formation of these compounds is low. Even the reaction of fluorine with liquid bromine gives rise to little evolution of heat, and if solid bromine is employed the reaction fails to take place; BrF changes easily to BrF_3 and free bromine. The combination of fluorine with iodine is rather more vigorous, but still not violent—iodine pentafluoride is fairly stable and does not decompose into its elements below 400°–500°. The effect of higher temperature is most noticeable in the formation of IF_7. The reaction $IF_5 + F_2 \longrightarrow IF_7$ is reversible; but whether the raising of the temperature only accelerates the establishment of an equilibrium or whether it favours the formation of IF_7 is not yet established. The former, however, is more likely. The compounds of iodine with chlorine and with bromine are naturally less stable; BrCl decomposes when vaporised. Even at −60° ICl_3 dissociates in the state of vapour into ICl and Cl_2, but ICl is only

[1] O. Ruff, E. Ascher and H. Krug, *Z. anorg. Chem.*, 1928, **176**, 270; 1930, **910**, 272.

slightly dissociated just above its boiling point, as is indicated by the observation that free iodine does not separate, although it is solid at the temperature at which the monochloride boils. The vapour of this compound, moreover, has an absorption spectrum which differs from that of free chlorine or of free iodine. The spectrum of iodine bromide vapour is also specific, but there is considerable dissociation, as might be expected from the similarity in properties between the two elements. The extent of decomposition cannot be found by determinations of the density, as the number of molecules is unchanged on dissociation, $2IBr \rightleftharpoons I_2 + Br_2$, but on analysis the vapour phase is found to contain excess of bromine and the residue excess of iodine. Thus iodine bromide cannot be distilled unchanged, and the dissociation is obvious even in the fused substance; the solidification curve, however, shows that it is without doubt a definite compound in the solid form.

The vapour of iodine trichloride is completely dissociated into the monochloride and free chlorine, and it is not possible to determine its melting point in an open vessel, as that of the monochloride is obtained instead. Even in an atmosphere of chlorine the trichloride is decomposed, as the dissociation pressure exceeds one atmosphere at the melting point. (Actually, the pressure of chlorine at the melting point ($101°$) is 16 atm., and a pressure of one atmosphere is developed at $64°$.) As can be foreseen, the trichloride also decomposes in dilute solution. Both the iodine chlorides are soluble in organic solvents and also in liquid SO_2 and NH_3, in $POCl_3$, $AsCl_3$ and SO_2Cl_2. The trichloride does not give a normal molecular weight in these solutions, not merely because it is dissociated into the monochloride and chlorine, but also on account of its ionisation. These solutions conduct the electric current, the iodine going to the cathode, chlorine to the anode. The chlorides thus appear to be true salts of iodine corresponding to the hydroxides $I(OH)$ and $I(OH)_3$ (cf. p. 385). Molten iodine monochloride is ionised in the same way, as are also the double salts of ICl (p. 244), and iodine is liberated at the cathode on electrolysis. In acetic acid solution the ions appear to be $I^{\cdot}$ and ICl_2'. A solution of ICl in bromoform, however, shows the normal depression of the freezing point.

The existence of a compound $BrCl$ was formerly taken for granted, because the solubility of chlorine in bromine was the same as if a compound containing equiatomic proportions had been formed at room temperature. When investigated at other temperatures the solubility relations and the melting point and freezing point curves appeared to show that only a solution of chlorine in bromine was present. If, however, the equiatomic mixture is allowed to freeze out at very low temperatures, the vapour pressure curve is different from that obtained with less highly cooled mixtures, so that at very low temperatures $BrCl$ appears to exist, the equilibrium with the free elements moving in the direction of dissociation as the temperature rises. The existence of

BrCl has been confirmed spectroscopically. Further, a mixture of bromine and chlorine halogenates unsaturated acids more rapidly than the separate elements. The hydrate $BrCl.4H_2O$, formed by passing Cl into Br under a layer of water,[1] is more stable below $18°$ than are the hydrates of Cl and Br.

Properties.—IF_7, ClF and ClF_3 are colourless gases; all three solidify to white masses. IF_5 is a colourless fuming liquid; BrF is red and BrF_3 is bright yellow with a greenish tinge. IBr is a hard crystalline mass like iodine, and BrCl is composed of crystals of an ochre-yellow colour. ICl and ICl_3 are solids, and exist in two modifications. Only the commoner form of ICl_3 has been studied; it consists of lemon to orange deliquescent needles. Both forms of the monochloride are easily obtained from the fused substance by varying the conditions of cooling. They are monotropic, and the brownish-red tables of the β-form are labile and pass readily into the ruby red needles of the α-form; both forms give the same liquid on fusion.

The reactions of these substances are mostly moderated reactions of the halogens they contain, but ClF_3 is more reactive than fluorine. The very reactive BrF_3 behaves like fluorine, and both IF_5 and IF_7 form fluorides with non-metals, but do not react with the same ease with metals, as they become coated with a protecting layer of fluoride. The iodine chlorides, similarly, behave as fairly active chlorinating agents; ICl_3 and ammonia give nitrogen iodide. ClF inflames cotton wool and filter paper in the same way as fluorine; but ClF_3 is a more powerful fluorinating agent and not only sets fire to organic materials and attacks many elements with explosion, but reacts with many oxides and decomposes water with a noise like the crack of a whip.

Water hydrolyses these substances, but very often further reactions take place among the products. The hydrolysis is reversible, thus: $ICl + H_2O \rightleftharpoons IOH + HCl$, and if excess of the halogen acid which is formed is previously added the hydrolysis is repressed. If no free HCl is present to begin with the IOH is rapidly transformed into iodate and iodide, but even at this stage the addition of acid reverses the reaction, as the iodate is reduced by the hydrochloric acid. The hydrolysis of ICl_3 is analogous; $I(OH)_3$ is first formed, but breaks down into iodate and hypoiodite: $2I(OH)_3 \longrightarrow HIO_3 + HIO + 2H_2O$. When, however, hydrochloric acid is previously added, ICl gives a pale yellow, ICl_3 a deep yellow solution. These solutions contain not only the chlorides dissolved as such, but also their compounds with HCl, which have not so far been isolated in the free state, though their salts are well known and correspond to the acids $HICl_2$ and $HICl_4$ (p. 244). Iodine bromide behaves in a similar way. The inter-relations of these substances with the polyhalides (p. 243) are interesting

[1] Anwar-Ullah, *J. Chem. Soc.*, 1932, 1176.

for the inter-halogen compounds are formed by the dissociation of polyhalides, e.g. $KI + Br_2 \longrightarrow KIBr_2 \longrightarrow KBr + IBr$ and some polyhalides can be formed by the reverse process : $MCl + ICl_3 \longrightarrow MICl_4$.

Oxyfluorides of Iodine.—The hydrolysis of iodine pentafluoride occurs in the following stages :

$$IF_5 \qquad IOF_3 \qquad IO_2F \qquad I_2O_5.$$

With excess of water, iodic acid is the main product, but if the reaction is partly reversed by the addition of hydrofluoric acid, IO_2F, or its complex with HF, $IO_2F \cdot HF$ or $\left[I \begin{smallmatrix} O_2 \\ F_2 \end{smallmatrix} \right] H$ is formed. When the presence of much water is avoided by the use of non-aqueous media, IOF_3 can be isolated. All these compounds are, however, more easily prepared by the reverse process of fluorinating I_2O_5 with HF. Fluoroiodates of the general formula $[IO_2F_2]M^I$ are obtained as colourless crystals from solutions of alkali iodates in concentrated hydrofluoric acid ; the more highly fluorinated compound $IOF_3,5H_2O$ is obtained from solutions of iodic acid in acetic and hydrofluoric acids ; while from alcoholic HF and HIO_3 the compound $IOF_3 \cdot H_2O \cdot C_5H_5N$ is obtained on addition of pyridine.

Only the caesium salt of fluorinated periodic acid is known. These compounds correspond to the fluorinated acids of the higher metallic oxides (p. 499).[1] No other fluorinated halogenates are known, nor are chlorinated iodates and bromates.

[1] Cf. Weinland, Z. anorg. Chem., 1898, **20**, 30 ; 1899, **22**, 256 ; 1908, **60**, 163.

III. OXIDES OF HYDROGEN AND OF THE METALS

CHAPTER XIV

WATER AND HYDROGEN PEROXIDE

Formation of water—Theories of oxidation—Isolation of deuterium oxide—Physical properties of water and of deuterium oxide—Chemical properties—Hydrogen peroxide

WATER

The Formation of Water and the Combination of Oxygen and Hydrogen.[1]—Oxygen and hydrogen confined in a glass vessel do not combine to a notable extent even at 100°. The reaction begins very slowly at 300°, and at higher temperatures the rate increases rapidly until finally the combination proceeds with explosion, which is one of the most violent in gaseous reactions, and often shatters the vessels in which it occurs. The reaction need only be started in a small fraction of the mixture, when it proceeds rapidly through the whole mass of gas—a minute electric spark is sufficient. The combination can, however, take place without explosion if the explosive mixture is allowed to stream from a jet at a greater rate than the velocity of the explosion wave. The latter is, however, very high (2820 m. per second) and it is easier to get the combination to take place by mixing the gases only when they come into the flame, as in the oxy-hydrogen blowpipe.

The combination is slowed down or stopped altogether if the explosive mixture is diluted with other gases. The molecules which do not take part in the reaction act as buffers and reduce the velocity of the explosion wave. Thus, even the admixture of excess oxygen reduces the explosion velocity, and although 1 vol. of detonating gas $(2H_2+O_2)$ mixed with 9.4 vols. of oxygen still explodes, it does not do so if 10.5 vols. are mixed with it. Even the slow non-explosive combination on sparking does not occur when less than $\frac{1}{100}$ vol. of hydrogen is mixed with 1 vol. of oxygen. Hence in gas analysis, when it is desired to determine the hydrogen in such mixtures, a known volume of hydrogen must be added to bring the total quantity of

[1] *Cf.* Dixon, *J. Chem. Soc.*, 1910, **97**, 661 ; 1911, **99**, 588.

hydrogen above the minimum, when on explosion the whole of the hydrogen is burnt. The movement of the explosion wave is also distorted by disturbances in the mixture, and thus it only explodes at 650°-730° when passed through a glass tube, while when the gas is stationary the explosion occurs at a much lower temperature—as low as 500° in smooth glass vessels. The minimum explosion temperature is not easily ascertained with certainty, owing to the effect of the walls of the containing vessel. This is less noticeable if the gas is heated internally by a known compression, from which the temperature can be calculated. In this way Nernst found the minimum temperature to be 550°. Dilution with other gases raises the ignition temperature, but the difference is not very marked unless the dilution is considerable. Thus in mixtures in which the proportions were varied between 0·5 and 6·0 vols. of hydrogen per volume of oxygen, the temperature of ignition varied only between 530° and 590° under the same conditions of experiment. The minimum was found to lie, not at the point corresponding to $2H_2 + O_2$, but in a mixture richer in oxygen.[1]

The temperature produced in the combination of oxygen and hydrogen may rise to 3100°. If complete combination of the gases occurred it should be much higher, but it is probable that only about one-third of the molecules combine at this temperature, as the equilibrium $2H_2O \rightleftharpoons 2H_2 + O_2$ is then largely displaced to the right. The dissociation of water in accordance with this equilibrium is observed at much lower temperatures, thus:

1397°	1561°	2257°	T.
0·0078	0·036	1·77	per cent. dissociated.

This dissociation can be shown by allowing a piece of white-hot metal to drop into water, when a quantity of detonating gas is liberated.

The explosion occurs at much lower temperatures in rough vessels than in those with smooth walls, and there are good grounds for supposing that, like many other slow reactions in gases, the combination of the two gases occurs at the surface of the containing vessel (cf. p. 520).

The catalysis of this reaction by all sorts of solid bodies is well known. The combination occurs rapidly below 350° in contact with carbon, sand, pumice, powdered glass and other materials with a large surface. Metals like cobalt, nickel, iron, copper, etc., accelerate the action still more, possibly owing to the formation and subsequent reduction of oxides of the metal. The formation of intermediate compounds can often be shown by the mechanical changes in the catalyst. Thus when water is synthesised with the use of a smooth silver gauze, the surface of the silver becomes roughened.[2] Such a catalyst is more active if it has been kept for a time in one of the gases,

[1] Mitscherlich, Z. anorg. Chem., 1916, 98, 145.
[2] Bone, Ber., 1913, 46, 13.

but this activity is soon lost. Probably the gas dissolves in the catalyst and then reacts under an over-voltage, in the same way as hydrogen liberated at a metal electrode in electrolysis.

The catalytic combination of oxygen and hydrogen is retarded by certain gases such as H_2S, CO, iodine vapour, and also by fats. With some substances, like CS_2, HCN, $HgCl_2$, the catalyst is poisoned and ceases to function (p. 109). The catalysis takes place very readily in contact with noble metals like gold and silver, but not with mercury, as the gases are not soluble in this metal. The platinum metals are most effective in speeding-up this reaction, and even at room temperature combination takes place rapidly if the metal is finely divided, but without inflaming the mixture. With platinum sponge, or still better with platinum black, the gases are ignited.

There is no doubt that the mechanism of the combustion of these gases is very complicated and much work has been done on it by Semenoff and by Hinshelwood and their collaborators.[1] The reaction velocity depends on the pressure and between certain definite limits is explosive. With increase of pressure the velocity slowly increases from A to B (Fig. 52); at B the reaction suddenly becomes explosive and remains so until pressure C is reached. Here the velocity suddenly falls and then increases regularly as indicated by CD.
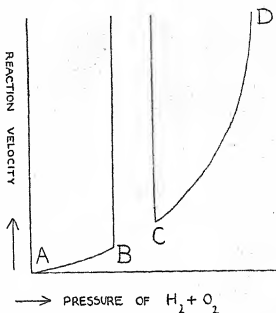
FIG. 52.

The combustion is considered to be due to OH radicals or H_2O_2 molecules. Alyea[2] considers that hydrogen and oxygen, adsorbed on the surface at low pressures, react and gaseous OH radicals are formed, which initiate the chain reaction:

$$OH + H_2 \longrightarrow H_2O + H$$
$$H + O_2 + H_2 \longrightarrow H_2O + OH$$
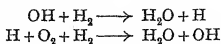
At low pressures the OH radicals are deactivated at the surface at a greater rate than that of the chain reactions; at higher pressures they are deactivated by collisions in the gaseous phase while at intervening pressures the above chain reaction ensues.

Grant and Hinshelwood postulate that H_2O_2 is the active material.

[1] *The Kinetics of Chemical Change in Gaseous Systems*, Oxford, 1933.

[2] *J. Amer. Chem. Soc.*, 1931, 53, 1324; 1933, 55, 3227.   *Cf.* Hinshelwood, Williamson and Wolfenden, *Proc. Roy. Soc.*, 1934 [A], 147, 48; Frost and Alyea, *J. Amer. Chem. Soc.*, 1934, 56, 1251.

It may, of course, react thus: $H_2O_2 \rightleftharpoons 2OH$, which would make the reaction mechanism very similar to that outlined above. In a silver vessel, which would destroy H_2O_2, the combination of H and O occurs entirely at the surface and no reaction takes place in the gaseous phase.

Hinshelwood, Moelwyn-Hughes and Rolfe found that the combination of D_2 and O_2 took place as a chain reaction in the gas phase at 560° under a pressure greater than the upper explosion limit. It proceeds at about 64 per cent. of the speed of the H_2—O_2 reaction.

Theories of Oxidation.—v. Wartenberg and Sieg[1] had previously postulated that the combustion of hydrogen takes place by the formation of H_2O_2 from H_2 and O_2, and as this product is not stable at the temperature of the flame it breaks down into H_2O and O. The ozone found in the resulting gases is held to be formed by the combination of the oxygen atoms that set free. It is necessary to distinguish between oxidations in the absence of water and the series of reactions which occur when it is present. Engler and his pupils[2] considered phenomena which he terms *autoxidations*—reactions in which the oxygen of the air only oxidises substances in aqueous solution when another oxidation takes place at the same time. Thus KI is not oxidised to iodine, nor arsenious acid to arsenic acid, nor is indigo-sulphonic acid bleached, unless turpentine is simultaneously oxidised by the atmospheric oxygen. All these substances are unaffected by the air if the turpentine is absent. Van 't Hoff and Jorissen had previously shown that the *autoxidator* (the turpentine) takes up the same quantity of oxygen as the *acceptor* (the KI, etc.), so that the oxygen is equally shared between the two substances. These observations are related to that of Moritz Traube, that the oxidation of zinc in water and air gives a quantitative yield of hydrogen peroxide, thus :

$$\text{Zn} + \begin{matrix} \text{OHH} \\ \text{OHH} \end{matrix} + \begin{matrix} \text{O} \\ \text{O} \end{matrix} \longrightarrow \text{Zn(OH)}_2 + \begin{matrix} \text{HO} \\ \text{HO} \end{matrix}.$$
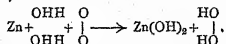
Engler found that in the absence of water twice as much oxygen is used up by the autoxidator and no oxidation of the acceptor takes place. Thus triethylphosphine $P(C_2H_5)_3$ combines with two atoms of oxygen per molecule when shaken with air, in the same way that alkali metals are converted direct to peroxides (Rb to RbO_2). On addition of water, oxygen is evolved and triethylphosphine oxide, $O\!\leftarrow\!\!-\!P(C_2H_5)_3$, is formed in the same manner as Rb_2O,H_2O ($=2RbOH$) is produced from the alkali metal. Thus the oxygen molecule is first added as a whole, and then one atom becomes attached to the acceptor :

$$\text{A} + O_2 \longrightarrow \text{AO}_2 ; \qquad\qquad \text{AO}_2 + \text{B} \longrightarrow \text{AO} + \text{BO}.$$
$$\begin{matrix}\text{Autoxi-}\\\text{dator}\end{matrix} \qquad\qquad\qquad\qquad \begin{matrix}\text{Accep-}\\\text{tor}\end{matrix}$$
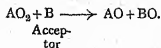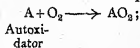
In the absence of another acceptor, a portion of the autoxidator which has not been oxidised may act as acceptor, and thus what appears to be a simple oxidation actually takes place as follows :

$$\text{A} + O_2 \longrightarrow \text{AO}_2 ; \qquad\qquad \text{AO}_2 + \text{A} \longrightarrow 2\text{AO}.$$
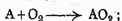
An acceptor is thus a substance which can only be oxidised with difficulty by ordinary oxygen, but which is readily oxidised by oxidising agents.

Engler distinguishes three forms of autoxidation. In the first kind a molecule of oxygen is added to the autoxidator, as has been described above for triethylphosphine. In the second the oxygen attacks the labile hydrogen of the autoxidator, forms hydrogen peroxide with it, and at the same time combines with the rest of the

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[1] *Ber.*, 1920, 53, 2192.   [2] *Ber.*, 1897, 30 ff., especially 1907, 33, 1097.

autoxidator (*e.g.* palladium hydride). In the third sort of reaction the autoxidator is not attacked after the H_2O_2 is formed, as in the oxidation of barium monoxide, though the product is not necessarily a peroxide. He also assumes an indirect form of autoxidation, of which the conversion of ferrous to ferric hydroxide is an example. The hydroxyl group of the water present is first attacked: $Fe(OH)_2 +$ $H \cdot OH \longrightarrow Fe(OH)_3 + H$, and the free hydrogen then combines with oxygen to form $H_2O_2 : 2H + O_2 \longrightarrow H_2O_2$, when the latter continues the oxidation. This type of reaction has been more fully investigated in the formation of ceric percarbonate, a red substance which is produced on aeration of solutions of cerous salts containing excess of potassium carbonate. The cerous carbonate first reacts with water in the same manner as ferrous hydroxide, with formation of hydrogen:

$$Ce_2(CO_3)_3 + 2H_2O \longrightarrow Ce_2(CO_3)_3 \!\! \begin{array}{c} \diagup OH \\ \diagdown OH \end{array} + 2H.$$
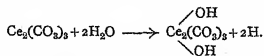
The hydrogen attaches itself to oxygen to form hydrogen peroxide, which then reacts with the original product, giving a perhydroxy-compound, from which the percarbonate is formed by dehydration, thus:

$$\begin{array}{c} \boxed{HO \qquad\qquad H} \cdot OOH \\ \diagdown Ce_2(CO_3)_3 + \\ \boxed{HO \qquad\qquad H} \cdot OOH \end{array} \longrightarrow 2H_2O + \begin{array}{c} HOO \\ \diagdown Ce_2(CO_3)_3 \\ HOO \end{array} \xrightarrow{-H_2O} O \!\! \begin{array}{c} \diagup O \\ \diagdown O \end{array} \!\! \begin{array}{c} O \diagdown \\ O \diagup \end{array} Ce_2(CO_3)_3.$$
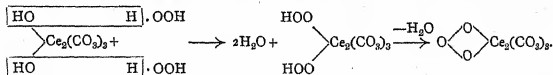
If an acceptor, such as arsenious acid, is present, it uses up the H_2O_2 and the higher cerium compound cannot be obtained. When the acceptor (*e.g.* grape sugar) can reduce the ceric compound to the cerous condition, the latter reacts once again with atmospheric oxygen and thus the cerous salt catalyses the oxidation of the sugar.

In this way reducing agents can act as oxygen carriers. Thus palladium hydride causes the oxidation of potassium iodide in the presence of air, owing to the formation of hydrogen peroxide as described above. Sodium arsenite is oxidised in the air only when sodium sulphite, normally a reducing agent, is present to act as autoxidator. The relation of reducing reactions to those of oxidation has been investigated in detail by Wieland,[1] who concludes that oxidations in the presence of water do not always proceed according to Engler's scheme, and instead of the direct addition of molecules of oxygen the abstraction of hydrogen takes place. Wieland investigated the hydrogenation of organic substances by the aid of palladium black.

Haber and Willstätter[2] have worked out an attractive theory which covers many cases of autoxidation and which has stood the test of experimental verification. They conclude that the first stage in these processes is the formation of a univalent radical, which then forms another univalent radical with the foreign molecule; this then reacts with the original molecule to reproduce the first univalent radical, and so the process continues as a chain reaction, similar to that which occurs in the union of hydrogen and chlorine (p. 216) or of hydrogen and oxygen. The following example illustrates the conception of these authors.

In the autoxidation of alkali sulphites in the presence of $Cu^{..}$, the first step is: $SO_3'' + Cu^{..} + H_2O \longrightarrow -SO_3H + Cu^{.} + OH'$. The radical $-SO_3H$ is thus liberated and at high dilutions it is very improbable that two of these will unite to form dithionic acid (p. 559); the more usual course is that of oxidation, thus:

$$-SO_3H + O_2 + H_2O + SO_3'' \longrightarrow 2SO_4'' + -OH + 2H^{.}$$
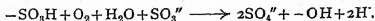
An $-OH$ radical is formed as well as the sulphuric acid, and so there is a fresh formation of $-SO_3H$ as follows: $-OH + SO_3'' + H^{.} \longrightarrow OH' + -SO_3H$, and so the

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[1] *Ber.*, 1912, 45, 484, and in the following volumes.　　　[2] *Ber.*, 1931, 64, 2844.

chain of reactions begins over again. If two of these radicals once combine to form dithionic acid, the sequence is broken, but Haber and Willstätter have calculated that the number of links in the chain of reactions is at least 10^6. In support of this theory there is the recently discovered fact that the life of free radicals is by no means so short as was previously supposed ; they are important factors in many organic,[1] biochemical and enzyme reactions—for some inorganic examples see H. Kauffmann.[2]

A special case of oxygen catalysis has been observed by K. A. Hofmann.[3] Potassium chlorate does not ordinarily act as an oxidising agent in neutral or weakly acid solution, but if very minute quantities of osmium tetroxide, OsO_4, are present it gives up all its oxygen. Hofmann suggests that a higher oxide of osmium is formed which acts as the oxidising agent and which is periodically oxidised by the chlorate.

Isolation of Deuterium Oxide (Heavy Water).

—The discovery of deuterium has opened up entirely new and important aspects in the chemistry of water. Whether of mineral, vegetable, animal or industrial origin, water shows in general only slight variations in D_2O content from I in 5000 parts.[4] The richest commercial sources of D_2O (about I in 3000 parts) are aqueous alkaline solutions which have been subjected to prolonged electrolysis,[5] for H_2 is evolved more readily than D_2. In one series of experiments NaOH was added to 2310 litres of water to make a 0·5 N. solution, which was then electrolysed using nickel electrodes. When the volume had thereby been reduced to 340 litres, the solution was treated with CO_2 in excess, the water distilled and subjected to further electrolysis after addition of NaOH until the volume was again reduced to about one-seventh of its initial value at this stage. The progress of the electrolysis is shown in the following table :

Stage.				Volume Electrolysed.	$d_{4^\circ}^{20^\circ}$ of Residue.	D_2O per cent. in Residue.
I.	.	.	.	2310 litres	0·998	0·03
II.	.	.	.	340 ,,	0·999	0·5
III.	.	.	.	52 ,,	1·001	2·5
IV.	.	.	.	10·15 ,,	1·007	8·0
V.	.	.	.	2 ,,	1·031	30·0
VI.	.	.	.	420 ml.	1·098	93·0
VII.	.	.	.	83 ,,	1·104	99·0

With continued electrolysis, the evolved gases become continually richer in D_2, so that in the later stages of the process they are recombined and again electrolysed.

Physical processes, such as fractional crystallisation, distillation or selective adsorption lead only to very partial separations. Pure D_2O is now a commercial product.

[1] See Pearson, *Ann. Rep. Chem. Soc.*, 1934, **31**, 240.   [2] *Ber.*, 1932, **65**, 179.
[3] *Ber.*, 1912, **45**, 3329 ; 1913, **46**, 1657.
[4] Eméleus, James, King, Pearson, Purcell and Briscoe, *J. Chem. Soc.*, 1934, 1207.
[5] Washburn and Urey, *Proc. Nat. Acad. Sci.*, 1932, **18**, 496 ; Lewis and Macdonald, *J. Amer. Chem. Soc.*, 1933, **55**, 3057 ; Taylor, Eyring and Frost, *J. Chem. Physics*, 1933, **1**, 823.

Physical Properties of Water and of Deuterium Oxide

As is indicated in the table below, there are very definite differences in properties between "ordinary" water, that is, the naturally occurring mixture of water and deuterium oxide, and "heavy" water or deuterium oxide.*

Both are colourless, odourless liquids, their other properties being as follows :

	Deuterium Oxide (D_2O)	"Ordinary" Water (D_2O, 1 ; H_2O, 5000)
Density ($d_{20°}^{20°}$)	1·10714	1·0000
B.pt.	101·42°	100·0°
M.pt.	3·82°	0·000°
Maximum density at . . .	11·6°	4·0°
Surface tension (dynes/cm.) . .	67·8	72·75
Viscosity (millipoises at 20°) .	1260	1009
Mol. heat of vaporisation (cals.) .	9969	9710
„ „ fusion (cals.) . .	1520	1436
Solubility at 25°, g./g. liquid :		
NaCl	0·297	0·358
$BaCl_2$	0·289	0·357
Ionic mobilities at 18° :		
K˙	54·5	64·2
Cl⁻	55·3	65·2
H˙ and D˙	213·7	315·2

Form of the Molecule.—The water molecule is not linear, as is definitely shown by measurements of its dipole moment. The angle between the two O—H bonds is 104° 31'. Pauling deduced the probable angle of 90° since the bond is formed by the p electrons of oxygen which would lead to bonds mutually at right angles. The observed deviation is explained by the partial ionic character of the bonds, which gives rise to small positive charges, and hence repulsion, on the hydrogen atoms. Similar angles (about 105—110°) are found in many cases, but in H_2S the value is only very slightly larger than 90° (92° 20').

The Forms of Water.—Ordinary ice is the only solid form stable at ordinary pressures, but several other kinds of ice can be obtained at high pressures. These have been investigated by Tammann,[1] and according to Bridgman[2] there are several varieties of ice :

Ice   I. 13·5 per cent. lighter than water—ordinary ice.
  „   II. 20 per cent. denser than Ice I.
  „   III. 3 per cent. denser than water.
  „   V. 5·5 per cent. denser than Ice III.
  „   VI. 4 per cent. denser than Ice V.

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* Unless otherwise stated, in this book by water is meant "ordinary" water.
[1] *Z. physikal. Chem.*, 1910, 72, 609.
[2] *J. Franklin Inst.*, 1914, 177, 315.

All these varieties are heavier than water except Ice I. (density 0·92). Ice is not easily compressible, and high pressures are produced when ice is formed from water in a closed space. So great is the force developed that shells of cast iron as much as one cm. thick are broken when filled with water and cooled to 0°. This effect is of great importance in nature, for when the water in fine cracks in rocks is frozen, the mass of rock is disintegrated. If, however, the water is compressed before freezing (to about 20,000 atm.) one of the other forms of ice is produced.

As ice is lighter than water, the freezing point is lowered by increase of pressure, in accordance with Le Chatelier's principle. The lowering of the freezing point by pressure is so slight that the ordinary variations in atmospheric pressure produce no appreciable effect. The vapour pressure of water at the triple point is 4·6 mm.

The *latent heat of fusion* of ice is high (79·15 cals./g.), due in all probability to a depolymerisation which takes place when the ice is fused. The X-ray analysis of ice shows that the lattice is polymolecular, and although complete depolymerisation does not take place at the melting point, a good many of the complex molecules decompose at this temperature. The hardness of ice is low, being only 1·5 on Moh's scale. The solid is blue in thick layers like water, which is seen to be blue in depths of above two metres, though it has been questioned whether the colour is due to the water itself. Pollution of the water may cause it to become colourless or to assume a different colour; for instance, the green colour of many mountain lakes is due to suspended calcium carbonate, and organisms of various kinds cause other colorations.

The *density* of water is at a maximum at 4°. It can be supposed that the natural contraction below 4° is masked by expansion due to the formation of "ice-type," $(H_2O)_3$ polymerised molecules. Similarly the maximum density of heavy water at 11·6° is due to $(D_2O)_3$ molecules. Taking the volume of water at 4° as unity, the volume at various temperatures is as follows:

0°	4°	10°	20°	30°	33°
1·000122	1·000000	1·000261	1·001741	1·004310	1·005266

The *compressibility*, like that of ice, is low. The *viscosity* of water decreases very rapidly with rise of temperature, and is actually eight times as great at 0° as at 100°—a point to be remembered in filtering and washing precipitates. If the requisite precautions are taken, both the freezing and the boiling of water can be delayed. For instance, when no trace of dissolved air is present, or in an evacuated vessel, the boiling of water does not take place below 182°, but it then vaporises explosively. The bumping of boiling liquids, particularly of alkaline liquids, is a familiar example of the effects of superheating of water.

If the boiling is interrupted during a molecular weight determination by Beckmann's method, the absence of dissolved gases prevents a definite boiling point being observed a second time.

The under-cooling of water takes place easily if the liquid is undisturbed, but crystallisation takes place rapidly if movement of the water occurs or if a crystal of ice is added. Water is not much polymerised in the state of vapour, though under high pressures the molecular weight is found to be somewhat high; e.g. 19·06 at 4 atm. instead of the normal value for H_2O (18·01). In the liquid state the molecular condition is more complex; in many organic liquids water is definitely bimolecular.

The mean molecular weight of liquid water can be determined in a variety of ways, of which the following are the more important:

1. The molecular volume of a liquid (v) can be calculated, given the critical temperature (t_k) and its surface tension (γ) at $t°$, from the expression [1]

$$v^{2/3} = \frac{2 \cdot 12(t_k - 6° - t)}{\gamma}.$$

The molecular weight is the product of mol. volume and density. The value for water is considerably above 18.

2. According to Trouton, if the molecular heat of vaporisation is divided by the boiling point in degrees absolute the quotient is approximately 20·63, when nothing more than a condensation of molecules from the gaseous to the liquid state is involved. For water the ratio is too high (25·9), the latent heat being augmented by the heat of depolymerisation of the molecules which are associated in the liquid state.

3. When the boiling point of water is compared with that of similar liquids (e.g. H_2S) it is much higher than would be expected. Indeed, to be in line with the similar hydrides, water should be gaseous at the ordinary temperature and liquefy at -100° (boiling point of H_2S, -6°). All these methods give further indications of the complexity of liquid water.

Bernal and Fowler[2] have suggested a "pseudo-crystalline" structure for liquid water, which accounts qualitatively and to some extent quantitatively for phenomena such as the variation of dielectric constant with temperature, the extent of hydration of ions, the viscosity of electrolytes and the mobilities of hydrogen and hydroxyl ions.

The density of water is much less than would be expected for a close-packed liquid with the known dimensions of the molecule; and from this, and from the X-ray diffraction curves of liquid water, these authors conclude that the molecules are arranged in a structure similar to that of the SiO_2 molecules in quartz. This arrangement (Water II) is the main constituent of the liquid between 0° and 100°. Undercooled water contains arrangements of the tridymite type (Water I), corresponding to the structure of ice itself. Above 100° and to an increasing extent as the critical temperature is approached, water passes into a close-packed form (Water III) characteristic of

[1] Eötvos; Ramsay and Shields, Z. physikal. Chem., 1893, 12, and foll. vols.
[2] J. Chem. Physics, 1933, 1, 515; Trans. Faraday Soc., 1933, 29, 1049.

an ideal liquid. The "pseudo-crystalline" forms differ from the crystalline in the continual fluctuations of the arrangement of the molecules. The complexity of water may be explained by the formation of hydrogen bonds, such that each oxygen atom is surrounded tetrahedrally by four other oxygen atoms. The distance O——O in ice is such as would be expected (2·76 Å) in the event of O—H......O bonds being formed; moreover, there is evidence that the position of the proton is not exactly midway between the oxygen atoms but resonates thus :—

$$
\begin{array}{ccccc}
\text{O} & 0.99 & \text{H} & 1.77 & \text{O} \\
\end{array}
$$

$$
2.76 \text{ Å}
$$

$$
\begin{array}{ccccc}
\text{O} & 1.77 & \text{H} & 0.99 & \text{O} \\
\end{array}
$$
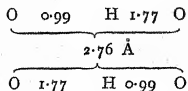
Water, when very pure, is a poor conductor of electricity, and the purest conductivity water has a *conductivity* of about 0.038×10^{-6} reciprocal ohms at $0°$. One mm. of water has the same resistance as 40 million kilometres of copper wire of the same cross-section, a length which would stretch round the earth a thousand times.[1] It has been calculated that 1 g. of hydrogen ions and the corresponding 17 g. of hydroxyl ions are contained in 13 million litres of water. The "hydrogen ion" in aqueous solution is probably the "oxonium ion":

$$H_2O \rightleftharpoons H^{\cdot} + OH'$$
$$H^{\cdot} + H_2O \rightleftharpoons [H_3O]^{\cdot}$$

or

$$2H_2O \rightleftharpoons [H_3O]^{\cdot} + OH'.$$
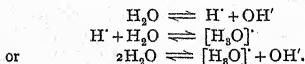
This view brings water, as an acid, into line with Hantzsch's suggestions (pp. 222 and 360). The ionic product $[D_3O]^{\cdot}[OH]'$ is smaller than the corresponding expression $[H_3O]^{\cdot}[OH]'$ for H_2O.

Water has a very high *dielectric constant* (81) and few liquids approach it in this property. This accounts for the great ionisation of salts, acids and bases in water. A few inorganic liquids (*e.g.* liquid ammonia and liquid sulphur dioxide) approach water in ionising power, but organic liquids cause little ionisation. No other liquid shows such regularity in the electrolytic dissociation of dissolved substances, and it is a fortunate circumstance that this cheap solvent is so applicable to all kinds of experimental work; possibly it may be said that water is the most fundamental material in the development of our system of chemistry.

The solvent power of water, quite apart from the property of ionising dissolved substances, is remarkable and water readily dissolves an exceptionally great variety of inorganic substances. This is partly due to the ease with which water combines with many of them, but sometimes no such simple explanation is found. The formation of hydrates usually increases the solubility, though the hydrates cannot

[1] Kohlrausch and Heydweiller, *Z. physikal. Chem.*, 1894, 14, 317.

always be isolated in the solid state, as the water of hydration is often so loosely attached that it is set free when an attempt is made to obtain the hydrate. This decomposition invariably occurs with solvated ions, the existence of which can be deduced from various electro-chemical properties of their solutions. The great solubility of hydrogen chloride, for example, can be explained by the assumption that either the ions or the undissociated molecules are surrounded by a loosely combined envelope of water (*cf.* p. 222). Bernal and Fowler (see p. 399) conclude that all univalent ions of radius less than $1\cdot6\,\text{Å}$ and all multivalent monatomic ions must be hydrated. The hydrated substances become similar to water in properties, and are miscible with it, for miscibility often depends on chemical similarity. This is noticeable even in the solid state, when compounds of similar structure form mixed crystals and are isomorphous with one another. It is still more pronounced in the liquid state; thus, metals may dissolve in molten metals without chemical reaction, sulphur in sulphur compounds, hydrocarbons in other hydrocarbons, etc. When, therefore, substances dissolve in water it is often on account of chemical similarity (*e.g.* they contain a hydroxyl group), or due to their combination with water which makes them approach water in their properties.

The relations between water and the dissolved substances become illuminated when heavy water is used as the solvent. For instance, when NH_4Cl is dissolved in water containing D_2O and then recovered, it has the same $H:D$ ratio as the water.[1] Further, if $[Co(NH_3)_6](NO_3)_3$ or $[Cu(NH_3)_4]SO_4, H_2O$ are dissolved in D_2O, all the H is exchanged for D; but if KH_2PO_2 is dissolved, no exchange occurs.

Gases are not very soluble in water unless combination occurs. The solubility of the commoner gases in 1 vol. of water at $0°$ and 760 mm. is as follows:

Gas:	He	H_2	CO	O_2	A	NO	N_2O	CO_2	Cl_2	HCl	NH_3
Vol. dissolved:	0·015	0·021	0·035	0·049	0·053	0·073	1·3	1·73	4·61	517	1299

The heat of solution of a gas is not necessarily due to the formation of compounds. The gas is compressed to a small volume, and this by itself causes evolution of heat. The solution of a solid or a liquid, on the other hand, is accompanied by a dilatation, as its volume is increased to that of the solvent, so that the solution of solids and liquids is normally accompanied by cooling. This absorption of heat is, however, frequently reduced and sometimes neutralised altogether by the heat evolved by other effects on solution. Among the positive heat effects are hydration, as discussed above, and ionisation, although the latter is often an endothermic process and is favoured by rise in temperature. The ionisation of some substances is exothermic, and then it decreases with rise of temperature. Hydrolysis is yet another effect which may make the heat change on solution more positive.

[1] Bonhoeffer and Brown, *Z. physikal. Chem.*, 1933 [B], **23**, 171.

Hydrolysis.—Hydrolysis is usually an incomplete reaction, thus:

$$AB + H.OH \rightleftharpoons A(OH) + HB.$$

The reaction can thus be detected by the appearance of an acid or alkaline reaction when a neutral substance is dissolved in water. For example, when aluminium sulphate dissolves in water, the following equilibrium is set up: $Al_2(SO_4)_3 + 6H.OH \rightleftharpoons 2Al(OH)_3 + 3H_2SO_4$ The $Al(OH)_3$ is a weak base and thus gives scarcely any OH' ions, but the H_2SO_4 is well ionised, and thus the solution has an acid reaction owing to the excess of hydrogen ions. This invariably happens when the salt of a weak base with a strong acid is dissolved. When the base is strong and the acid weak the solution is alkaline; *e.g.*: $Na_2CO_3 + 2H.OH \rightleftharpoons 2NaOH + H_2CO_3$.

When the solubility of the free acid or base produced is low, enough may be formed by the hydrolysis to give a precipitate. More must then be formed to maintain the equilibrium, and this process will continue until the quantity remaining in solution does not exceed the solubility product, when the hydrolysis will be brought to a standstill. Sometimes this end-point is not reached until almost all the salt is hydrolysed (bismuth salts), but with other substances it is attained before the product is visible to the naked eye, as it exists in the solution in colloidal form (Al and $Fe^{...}$ salts). The hydrolysis can then be made to proceed by coagulating the sol or by dialysing out the free acid. Thus solutions of aluminium salts remain clear when treated with sodium acetate, but, on heating, the basic acetate separates and does not redissolve to any great extent on cooling, although the hydrolysis is less in the cold.

Almost all salts are hydrolysed in solution, except those of the alkalis and of the strongly basic alkaline earths with strong acids. When a precipitate appears it is frequently not the hydroxide of the metal but a basic salt of such low solubility that the hydrolysis does not continue to the hydroxide stage. If the acid liquid is filtered off and the precipitate digested with fresh water, hydrolysis proceeds again and eventually the pure hydroxide may be obtained. As may be expected, the products of hydrolysis seldom have a composition corresponding to a known compound (*e.g.* commercial basic bismuth nitrate). The degree of hydrolysis can be deduced from measurements of the H ion concentration of the solution.

Hydrolysis is not confined to salts or other bipolar compounds but occurs with homopolar substances also; compare, for example, the hydrolysis of chlorine to HCl and HClO (p. 362) and the hydrolysis of sulphur and phosphorus (pp. 543 and 713). D_2O is generally less reactive chemically than H_2O—for instance, D_2O reacts with Al_4C_3 about twenty times more slowly than water, forming heavy methane CD_4.

Hydrates.—The formation of additive compounds with many sub-

stances is also an important property. The numerous crystals with water of crystallisation all contain combined water, and are complex compounds of which the nature has already been discussed on pp. 269, 276, 328. The complexes are often weak, and the crystals effloresce in the air if the pressure of aqueous vapour of the crystals is greater than the ordinary vapour pressure of water in the air (*cf.* p. 270). On the other hand, the water is sometimes so firmly combined that the hydrate is regarded as a primary valency compound. Sulphuric acid is an example of a very stable hydrate; it is formed from sulphur trioxide and water, and is decomposable into these components: $SO_3 + H_2O \rightleftharpoons [O(SO_2)]H_2$. In fact, 100 per cent. H_2SO_4 gives off some SO_3 spontaneously, but it also behaves in some respects as if both the hydrogen atoms were directly connected with oxygen atoms, and it is probable that an equilibrium of the type $[O(SO_2)]H_2 \rightleftharpoons SO_2(OH)_2$ exists.

The hydrates, in general, are similar in properties to the ammines. The ammonia, however, is usually attached to the metallic constituent of the molecule, while the water can be closely attached to the negative part, or even to both parts at the same time. The regularities in structure and behaviour are thus recognised less easily in the hydrates than in the ammines, and the number of water molecules is more variable. For example, in the vitriols the sulphates of the bivalent metals have 7 or 5 mols. of water, whereas these numbers of ammonia molecules are but seldom found in the ammines. The attachment of the water to the acid radical as well as to the metal is due to the fact that both the oxygen and the hydrogen are linked up, whereas in the ammines it is usually the nitrogen and very seldom the hydrogen which is so attached. The irregularities of hydrate formation are discussed when dealing with the compounds concerned.

It is remarkable that the elements are seldom hydrated, and their general insolubility in water is connected with this property. The absence of polar character in the molecules of the elements is probably the cause of this lack of affinity for water. These polar differences are most notable in the halogens, and the solubility and hydrolysis of chlorine and bromine are the consequence of this property.

100 g. water dissolve at	0°	10°	20°	
	1·5	1·0	0·8	g. Cl_2
	4·2	3·7	3·6	g. Br_2

These elements also form hydrates, the formulae of which, according to Roozeboom,[1] are $Cl_2,6H_2O$ and $Br_2,10H_2O$. Both hydrates are obtained by cooling the saturated solutions. Chlorine hydrate forms yellow crystals, bromine hydrate red masses or octahedra; the dissociation pressure reaches one atmosphere at 9·6° and 6·2° respectively,

[1] *Rec. trav. chim.*, 1885, 4, 65.

and above these temperatures the hydrates cannot be kept in open vessels. Chlorine hydrate melts at 28·7° in a closed vessel, and then forms two layers—a solution of water in the hydrate and a solution of the hydrate in water. The latter contains 3·69 g. of chlorine to 100 g. of water. The stability of bromine hydrate in the presence of foreign gases is interesting, for it depends on the solubility of bromine vapour in the gas. The bromine is, for example, more soluble in oxygen than in hydrogen. Hence bromine hydrate is stable in oxygen at 20° at 150 atm., whereas in hydrogen it begins to decompose at 9° under a pressure of 200 atm.[1] Bromine hydrate decomposes into ice and bromine at −0·3°, just like the hydrate of HBr (p. 226).

The hydrates of the inert gases have been described on pp. 61 and 302. Many compound gases such as SO_2, H_2S, N_2O, ClO_2, also unite with water. PH_3, AsH_3, H_2Se, CO_2, as well as many organic gaseous compounds such as CH_4, C_2H_4, CH_3Cl, also combine with water to form hydrates, mostly containing $6H_2O$ and decomposing below 0° at atmospheric pressure.

Deuterates are formed in a similar manner to hydrates. The dissociation pressure is lower than that of the corresponding hydrates.

The Action of Water in Allotropic Changes.—It is well known that the presence of small quantities of water is essential for the progress of many, if not of all, chemical reactions. For instance, the alkali metals do not react with dry chlorine, and oxidation in general often takes a different course when water is present from that which occurs in its absence (p. 394). It is, however, very remarkable that the physical properties such as surface tension, boiling point, vapour pressure, and even the molecular weight derived from the vapour density are different for many substances according to whether water is present or carefully excluded. These differences appear when the substances are subjected to intensive drying[2] with phosphorus pentoxide for some years or at least for many months. After this treatment nitrogen trioxide, for instance, boils at +43° instead of −2°; nitrogen tetroxide has a much higher vapour pressure at a given temperature than usual, as the equilibrium $N_2O_4 \rightleftharpoons 2NO_2$ is displaced in favour of formation of NO_2. The boiling point of bromine after nine years' drying is found to have risen from 63° to 118°, that of mercury from 358° to 425°. Reaction with the P_2O_5 was excluded and there was also no question of overheating. The melting points of solids were raised by 2-5°, that of sulphur, for instance, from 112·5° to 117·5°. According to Smits there

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[1] This phenomenon of the increased solubility of vapours in other gases is of frequent occurrence. Thus, when a mixture of hydrogen and nitrogen in the proportions 3 : 1 is compressed over liquid ammonia, there is six times the theoretical quantity of ammonia in the gas phase. Again, iodine is more volatile in CO_2 than *in vacuo.* This effect is due to the action of field valencies (p. 302).

[2] F. B. Baker, *J. Chem. Soc.*, 1912, 51, 2339 ; 1922, 121, 568. A. Smits, *Z. physikal. Chem.*, 1927, 129, 33.

is an equilibrium between the different polymers in the substances, which is affected by the presence of water as a catalyst, and in its absence is displaced and stabilised under the new conditions. On addition of minute quantities of water the original properties of the substances immediately reappear.

HYDROGEN PEROXIDE

Hydrogen peroxide is formed by the direct addition of an oxygen molecule to hydrogen, or by the hydrolysis of compounds containing an —O—O— linkage. If a hydrogen flame burning in air is allowed to impinge on a block of ice, considerable quantities of hydrogen peroxide are found in the water produced; if the flame is not chilled the H_2O_2 is decomposed. The equilibrium between hydrogen and oxygen indicates that the endothermic hydrogen peroxide will be produced in quantity at the temperature of the oxyhydrogen flame. The proportion of hydrogen peroxide (0.74 per cent.) in the products of combustion is in agreement with the theoretical quantity formed at the temperature of the flame. When formed at lower temperatures, although the equilibrium mixture is less rich, the rate of decomposition is also lower. When air is passed over palladium saturated with hydrogen the peroxide is formed, as also when a stream of air is passed over a silver cathode at which hydrogen is being evolved. It is notable that hydrogen peroxide is formed by the reduction of oxygen and not by the oxidation of water.[1] Nascent hydrogen is also oxidised by atmospheric oxygen as in the oxidation of zinc in water mentioned on p. 394, where the hydrogen acts as autoxidator when an acceptor which acts rapidly is present. Thus in the presence of potassium cobalto-cyanide, which is converted into the cobalti-compound, or of indigo white, which is transformed into indigo blue, the oxygen is removed from the autoxidator.[2]

A different form of hydrogen peroxide, possibly $\begin{array}{c} H \\ \diagdown \\ \diagup \\ H \end{array} O \rightarrow O$, is produced by the interaction of atomic hydrogen and oxygen at the temperature of liquid hydrogen.[3]

The above methods of preparation do not give useful quantities of hydrogen peroxide, and the hydrolysis method is more commonly used. The most important groups of compounds with the —O—O— linkage are the per-acids and certain peroxides. Both these groups give hydrogen peroxide on hydrolysis:

[1] Traube, *Ber.*, 1893, **26**, 1471.
[2] Manchot, *Ann.*, 1901, **314** and **316**.
[3] Gerb and Harteck, *Ber.*, 1932, **65** [B], 1551.

$$SO_2 \diagdown^{OO.H}_{OH} + H_2O \longrightarrow SO_2 \diagdown^{OH}_{OH} + HO.OH.$$
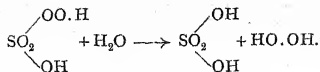
Permonosulphuric or Caro's acid.

$$HO.SO_2.O—O.SO_2.OH + 2H_2O \longrightarrow 2H_2SO_4 + H_2O_2.$$

Perdisulphuric acid.

$$Ba \diagup^{O}_{O} \Big| + \begin{matrix}H.OH\\H.OH\end{matrix} \longrightarrow Ba \diagup^{OH}_{OH} + \begin{matrix}OH\\OH\end{matrix}$$
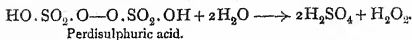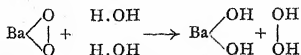
These reactions are reversible, and the hydrate of barium peroxide (p. 423) is obtained from barium hydroxide and hydrogen peroxide.

The peroxides of the alkali metals and of the alkaline earth metals are amenable to this hydrolysis. The dioxides of lead and manganese, PbO_2 and MnO_2, are not true peroxides, as they do not give hydrogen peroxide on treatment with acids. It can be supposed that in the former type of oxide the two oxygen atoms are in direct connection with one another, thus: $M \diagup^{O}_{O} \Big|$, but in such oxides as PbO_2 the metal is quadrivalent, thus, $O:M:O$. The second kind are sometimes described as superoxides.

Barium peroxide is the most useful substance for the preparation of hydrogen peroxide, as the by-products are then easily removed. The calculated quantity is added to sulphuric acid of such dilution that a 3 per cent. solution of H_2O_2 will result : $BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$. The barium sulphate is removed by filtration or decantation, and the H_2O_2 can then be concentrated, although the 3 per cent. solution is ordinarily employed in medicine and for industrial purposes. If the solution is made slightly alkaline with sodium carbonate the H_2O_2 can be extracted with ether. After removing the ether the liquid is again neutralised, and further concentration is only possible in the absence of salts of heavy metals and of substances which decompose H_2O_2 catalytically. The solution is further concentrated by freezing, when the H_2O_2 remains liquid ; it is then again extracted with ether, and finally concentrated by distillation *in vacuo*. In this way a solution containing 99 per cent. of H_2O_2 can be prepared, and further concentration can be brought about by freezing a small quantity in a mixture of ether and solid carbon dioxide and seeding the main bulk with the crystals thus obtained.

An important method of manufacturing H_2O_2 is based on the hydrolysis of dipersulphuric acid. After the formation of this acid by electrolysis of $KHSO_4$ (see p. 592) the H_2O_2 is distilled off *in vacuo* and the acid salt regenerated. Concentrations up to 30 per cent. can be obtained by this method.

Concentration can also usefully be effected by mixing the hydrogen peroxide solution with certain indifferent organic liquids and distilling.[1] Thus by mixing 1 part with 2 parts of xylene and distilling under ordinary pressure, the concentration of H_2O_2 in the residue is raised from 3 to 30 per cent. ; if a 30 per cent. solution is mixed with *p*-cymene and distilled under reduced pressure, the residue in the distillation flask is 90 per cent. H_2O_2. On cooling this in a mixture of ice and salt, crystalline anhydrous H_2O_2 is obtained.

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[1] Hurd and Puterbaugh, *J. Amer. Chem. Soc.*, 1930, 52, 950.

If not seeded, hydrogen peroxide can be highly under-cooled. The crystals melt at $-0.89°$ to a liquid which, like water, is colourless in thin layers, but blue in thicknesses above one metre, the colour being rather deeper than that of water. The pure liquid is syrupy ($d = 1.4649$) and is miscible in all proportions with water, alcohol or ether. It boils at 69° under a pressure of 29 mm.; by extrapolation the temperature of $151.4°$ is obtained for one atm. pressure—not much above the corresponding boiling point of water. Decomposition takes place slowly unless stimulated, but shaking is enough to start the evolution of oxygen. If violently rubbed or touched with oxidisable substances the liquid explodes. Wool is set alight when H_2O_2 is dropped on to it, and the decomposition of the 99 per cent. H_2O_2 is accompanied by violent explosion when it is dropped on to platinum black or manganese dioxide. More dilute solutions than 90 per cent. do not explode, but decompose rapidly in contact with certain substances (see below), especially if they are alkaline. Strong solutions must not therefore be kept in glass bottles, as these give up alkali, and bottles of paraffin wax are commonly used.

The dielectric constant of hydrogen peroxide (84.7) is even higher than that of water, and it is likely, therefore, that ionisation will also be great in this liquid. Weak acids are more highly dissociated in it than in water, and the ionisation of salts is also greater than in water. The pure liquid is a slightly better conductor than water, so that H· and OOH′ ions must be present. It is thus an acid but a very weak one. The true peroxides can be regarded as salts of H_2O_2, and the ease with which they are hydrolysed is a further indication of the weakness of H_2O_2 as an acid. Acid salts of H_2O_2 are also known—for example, the compound $NaO . OH$.

The polymerisation which liquid hydrogen peroxide shows, but which disappears in the vapour, is rather greater than that of water. Its constitution has not yet been fully elucidated. The formula $HO . OH$ is commonly used, with the assumption that the oxygen is bivalent and that the compound is really di-hydroxyl. It is not easy to account for the formation of H_2O_2 in the combustion of hydrogen by this formula, and optical and other physical properties do not indicate the presence of two bivalent oxygen atoms. The form $H_2O \longrightarrow O$ (see p. 405) appears to exist below $-115°$ and a co-ordination formula $[H(O_2)]H$ has also been suggested. In all probability the structure of the free acid is different from that of its salts—the former being a pseudo-acid (p. 361), the latter true salts. This would account for the greater ease of decomposition in alkaline solution.

The work of Bredig and his collaborators[1] on the *decomposition* of hydrogen peroxide is very interesting. The reaction is not markedly accelerated by light, but colloidal solutions of the metals affect it in

[1] See, for example, *Z. physikal. Chem.*, 1899, 31, 258 ; 1901, 37, 1.

a remarkable manner. Silver, gold, platinum and palladium sols are effective, the catalytic action increasing in that order. Even platinum black decomposes H_2O_2 with vigour. Bredig has suggested that the rate of decomposition at the surface is very rapid and that the observed rate is due to the slowness with which diffusion takes place. As the metal is always regenerated, the smallest quantities suffice for the continuous decomposition of large quantities of the peroxide. Thus a solution containing only 1 g. of Pd in 260,000 litres of water can still catalyse the decomposition of H_2O_2, if it is weakly alkaline. In a concentrated solution even chemically indifferent materials, such as sand, accelerate the decomposition, but it proceeds still more quickly if the catalyst starts an intermediate reaction; this is probably what happens in the catalytic decomposition of H_2O_2 by manganese dioxide: in acid solution the MnO_2 is reduced to the manganous salt by H_2O_2 with the liberation of oxygen and the reaction comes to a definite end. In alkaline solution the peroxide reoxidises the manganous hydroxide to a higher oxide, which again yields oxygen with H_2O_2, is again reduced, and so on, so that as long as there is still some H_2O_2 present the catalysis does not stop. Cobaltic hydroxide acts just like MnO_2.

The catalysis taking place with metallic mercury is peculiar, for decomposition and equilibrium take place rhythmically, if the solution possesses a certain, very slight alkalinity. The alternate appearance and disappearance of a yellow skin on the metal suggests that the following process takes place: the mercury is first oxidised by the H_2O_2 to an oxide (? HgO_2), then this is reduced to mercury by the H_2O_2 with double decomposition. As a matter of fact, yellow HgO is reduced to the metal on treating with H_2O_2 in alkaline solution, while the metal is oxidised to the oxide in acid solution. The rhythm is due to the alternating formation of a weakly acid and weakly alkaline solution.[1]

The fact that an oxidising agent acts here as a reducing agent leads to the assumption of an unstable intermediate stage. The same phenomenon also occurs in the action of acid H_2O_2 on MnO_2, and by treating an acid $KMnO_4$ solution with H_2O_2 the permanganate is converted to a manganous salt, with decolorisation and formation of oxygen. The reaction between chromic acid and H_2O_2 gives a hint of the process in this reaction; in acid solution a blue perchromic acid is formed, which is very unstable and is easily reduced to chromate and finally to tervalent chromium. It is therefore very likely that both the permanganate and the mercuric oxide form unstable higher oxides as intermediate products. The final reaction between permanganate and hydrogen peroxide is represented by the following equation:
$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 8H_2O + 5O_2.$$
The reaction can be used for determining either permanganate or

[1] See Hedges and Myers, *The Problem of Physicochemical Periodicity*, London, 1927.

hydrogen peroxide quantitatively, either by titration in the usual way or by measuring the evolved oxygen in a nitrometer.

The catalysis of hydrogen peroxide by platinum black, according to the work of Wieland,[1] takes place in the following stages :—The peroxide is first dehydrogenated : $H_2O_2 \longrightarrow O_2 + 2H$; the hydrogen then reacts with a second molecule of H_2O_2: $2H + H_2O_2 \longrightarrow 2H_2O$. The first reaction takes place at a measurable rate, the second practically instantaneously. The detail of this reaction is obtained by diverting the hydrogen to another acceptor, such as a persulphate, which reacts with H_2O_2 thus : $K_2S_2O_8 + H_2O_2 \longrightarrow 2KHSO_4 + O_2$.

When colloidal silver is the catalyst, Wiegel[2] supposes that there is a formation of AgOOH as an intermediate stage, as the dispersed silver is appreciably soluble in H_2O_2. When the solubility product of this peroxide is exceeded oxygen begins to come off; the silver is precipitated on to the microns already present, giving the sequence of colours mentioned on p. 104.

Whenever the decomposition is catalysed by metals the catalyst is liable to the phenomena of poisoning (Bredig), which have been discussed previously. Very slight quantities of certain substances, curiously enough mostly those which are also strong poisons for the human organism, make the catalyst inactive, but it is capable of recovering again if an insufficient quantity of the poison be used, and then often acts even more strongly than before. Such poisons are, for instance, PH_3, AsH_3, $HgCl_2$, and particularly HCN, of which 0·005 mol. can render inactive 1 atom of Pt.

Chemically, H_2O_2 is a strong oxidising agent, but as such acts best in alkaline solution, where for instance it at once converts the hydroxides of bivalent iron and cobalt into the tervalent, and that of manganese into the quadrivalent form, while alkaline chromic salts are oxidised to the chromate. Changes like that of ferro- and cobalto-potassium cyanide to the higher complex compounds take place very quickly with H_2O_2. On account of its oxidising action it is used as a bleaching agent and disinfectant. The oxidation of potassium iodide by H_2O_2 has been the subject of much investigation. This reaction, which causes the liberation of free iodine, though delicate, is very slow, and is a reaction of the first order. It is assumed that hypiodite is formed as intermediate product : $H_2O_2 + I' = H_2O + IO'$ by the unimolecular decomposition of H_2O_2; then in an immeasurably short time a second reaction takes place : $H_2O_2 + IO' = H_2O + O_2 + I$.

In neutral solution the reaction is greatly accelerated by the presence of $FeSO_4$, and in acid solution by molybdic acid, which gives a per-acid as intermediate product.[3] Starch iodide paper is thus a very delicate

[1] *Ber.*, 1921, 54, 2361. [2] *Z. physikal. Chem.*, 1929, 143, 81.

[3] Noyes and Scott, *Z. physikal. Chem.*, 1895, 18, 118 ; Bredig and Walton, *ibid.*, 1904, 47, 185.

reagent for H_2O_2, especially in acid solution. Still more delicate are the colour reactions of certain acids in which the per-acids of the metals are formed. The hydrolysis of per-acids is a reversible reaction :

$$X . OOH + H . OH \rightleftharpoons X . OH + HO . OH.$$

The colour therefore appears when H_2O_2 is added to the solution of the simple acid or even to the solution of a lower oxidation compound. Coloured per-acids are given by chromium, molybdenum and tungsten, and especially by titanium (for these per-acids see pp. 514, 843). Per-titanic acid, which is formed when H_2O_2 is added to a solution of a titanium salt in sulphuric acid, gives a brilliant yellow to reddish yellow colour, which serves to detect one part of H_2O_2 in 1,800,000. The colour is, however, bleached by fluorides.

The decomposition of H_2O_2 with evolution of oxygen also takes place on the addition of chlorine or of hypochlorites: $Cl_2 + H_2O_2 \longrightarrow 2HCl + O_2$; $CaCl . OCl + H_2O_2 \longrightarrow CaCl_2 + H_2O + O_2$. The chlorine and hypochlorite here react as reducing agents—the reactions probably proceed like that with permanganate.

Hydrogen peroxide can be attached to salts in the same way as water; but water of crystallisation is preferentially taken up even from concentrated solutions. In alum, for instance, only a small part of the water of crystallisation is replaceable by H_2O_2; it also forms compounds with calcium chloride and with potassium carbonate. Sometimes, as in perborax (p. 843), it is not a mere matter of the formation of an addition compound but a complete change in constitution which takes place. The per-acids, formed by the action of H_2O_2 on the acid anhydride, are further examples of the more profound change, *e.g.* :

$$SO_3 + H_2O_2 \longrightarrow SO_2(OH)(O . OH),$$
$$2SO_3 + H_2O_2 \longrightarrow SO_2(OH) . O . O . SO_2(OH).$$
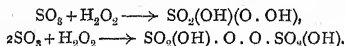
Hydrogen peroxide can form additive compounds with other anhydrides such as P_2O_5 (p. 730). When ethereal solutions of H_2O_2 and ammonia are mixed at low temperatures, ammonium peroxide, $(NH_4)_2O_2, H_2O_2$, crystallises. The corresponding water compound is unstable. The regular crystals melt when the temperature is allowed to rise, ammonia being set free.[1] There is also a stable compound of hydrogen peroxide with urea, $CO(NH_2)_2 , H_2O_2$.

Deuterium Peroxide

Deuterium peroxide can be prepared[2] by blowing deuterium oxide vapour through a mixture of deuterosulphuric acid and potassium persulphate at 70°–90°. The mixture of D_2O and D_2O_2 is fractionally condensed and enriched in D_2O_2 by further fractionation until 100% D_2O_2 is obtained.

[1] Melikoff and Pissarjewsky, *Ber.*, 1897-98, 30-31.
[2] F. Feher, *Ber.* 1939, 72, 1789.

OXIDES OF THE ALKALI AND ALKALINE EARTH METALS: THE RARE EARTHS

Oxides of the alkali metals—Hydroxides—Peroxide hydrates—Oxides of the alkaline earth metals—Peroxides—Hydroxides—The rare earths—Hafnium

Oxides of the Alkali Metals

THE following oxides of the alkali metals are known:

Li_2O	Li_2O_2		
Na_2O	Na_2O_2	*Na_2O_3*	
K_2O	*K_2O_2*	*K_2O_3*	K_2O_4 (= KO_2)
Rb_2O	*Rb_2O_2*	Rb_2O_3	Rb_2O_4 (= RbO_2)
Cs_2O	*Cs_2O_2*	*Cs_2O_3*	Cs_2O_4 (= CsO_2)

Those printed in italic have been obtained only by treating with oxygen solutions of the metal in liquid ammonia; the others can be obtained in other ways.

Only lithium gives an oxide of the type M_2O when the metal is burnt in air; with the other metals the highest oxide not printed in italic is formed. The lower oxides are formed only when excess of the metal is present or when the higher oxide is reduced by the metal: $Na_2O_2 + 2Na \longrightarrow 2Na_2O$, or $2NaOH + 2Na \longrightarrow 2Na_2O + H_2$. Na_2O is also obtained[1] by heating sodium nitrate or nitrite with sodium azide: $NaNO_3 + 5NaN_3 \longrightarrow 3Na_2O + 8N_2$.

After lithium, sodium forms a monoxide most readily, but if the reaction takes place in the cold there is not a sufficient local excess of unoxidised metal to prevent the formation of the higher oxide. If, however, the metal is burned in an insufficient supply of oxygen, the vapour of the metal can reduce the higher oxide which is first formed. The higher oxide is always contaminated with some Na_2O, and on heating the product of combustion *in vacuo* some free metal can always be distilled off from it.

The oxides of sodium and lithium of the type M_2O are white amorphous powders, that of potassium is yellowish, of rubidium bright yellow, of caesium orange red. The colour thus becomes deeper with increasing atomic weight. They are volatile at high temperatures, though Cs_2O vaporises markedly at 250°. It is decomposed into metal and peroxide at higher temperatures.

All these metals, with the exception of lithium, tend to form higher oxides, and even when lithium is burnt the product contains small quantities of Li_2O_2. Lithium is closely related to the metals of the

[1] Zintl and v. Baumbach, *Z. anorg. Chem.*, 1931, 198, 88.

alkaline earths in many properties and forms a link between them and the alkali metals. Thus its hydroxide, LiOH, and also its carbonate, like those of calcium, are decomposed at red heat according to the equations: $2LiOH \longrightarrow Li_2O + H_2O$ and $Li_2CO_3 \longrightarrow Li_2O + CO_2$, and if the water or carbon dioxide is removed from the equilibrium mixture by a current of an indifferent gas, a complete change to Li_2O takes place. Again, lithium, like the alkaline earths, has a lesser tendency to form higher oxides, while the hydroxides of the heavier alkali metals are converted into peroxides under a high pressure of oxygen. The compound Li_2O_2 is not obtained by the action of free oxygen like the calcium compound, but by dehydrating the peroxide compound $Li_2O_2, H_2O_2, 3H_2O$. Lithium monoxide, like burnt lime, is only slowly hydrated by water, while the corresponding oxides of the alkali metals react with great energy, thus : $M_2O + H_2O \longrightarrow 2MOH$. Li_2O is also distinguished by its high heat of formation (p. 441).

On burning in excess of oxygen the alkali metals yield as chief or sole products the following oxides: Li_2O, Na_2O_2, K_2O_4, Rb_2O_4, Cs_2O_4. These oxides do not all decompose on heating with evolution of oxygen —only Cs_2O_4 does this, and then with difficulty, being converted into Cs_2O_3. The others melt the more easily the higher the atomic weight of the alkali metal. K_2O_4 melts at a high temperature to a black oil, but Rb_2O_4 melts easily. On cooling, the crystals settle out again— those of Rb_2O_4 as plates. The depth of colour also increases with increasing molecular weight: the lithium compound is white, that of sodium slightly yellowish ; K_2O_4 is orange yellow, Rb_2O_4 dark brown.

Comparable substances are found in the peroxides of the alkaline earths, CaO_4 and BaO_4 (p. 421), also in the well-known BaO_2. Oxides of the formula M_2O_2 can be regarded as salts of H_2O_2, while those of the formula M_2O_4 can be considered as compounds of a higher order and written M_2O_2, O_2. It is questionable whether the formula M_2O_4 is not better halved. There is little to be said against the formulation MO_2. Both magnetic measurements and X-ray analysis agree with the simpler formula, but in this compound, magnetic measurement cannot be used to decide between the two formulations.[1]

The intermediate oxides in the table on p. 411 are obtained, as already mentioned, by treating a solution of the metal in liquid ammonia with oxygen.[2] The ammonia solutions of the metals are coloured deep blue (*cf.* p. 623), and if, for example, that of Cs is shaken with oxygen, a colourless or pale pink bulky precipitate settles out, while the solution is decolorised. The precipitate consists of the compound Cs_2O. If the shaking is continued without filtering off, this precipitate becomes of a chocolate brown colour and has the composition Cs_2O_3 at the maximum coloration. It is crystalline and melts on heating, when it becomes black. If the oxidation is continued further, the precipitate finally becomes yellow, forming needles of Cs_2O_4.

[1] Neumann, *J. Chem. Physics*, 1934, **2**, 31 ; Kassatockin and Kotov, *ibid*, 1936, **4**, 458 ; Klemm, *Z. angew. Chem.*, 1935, **48**, 617.
[2] Renegade, *Ann. Chim. Phys.*, 1907 (8), **2**, 416.

The reaction proceeds similarly with other alkali metals. With sodium the highest oxidation product is the pink compound Na_2O_3, which with water gives Na_2O_2 and oxygen; potassium gives a sulphur-coloured precipitate, K_2O_2, and later on red K_2O_3 is formed; both are gelatinous precipitates. From rubidium the yellow crystalline Rb_2O_2 and the black Rb_2O_3 are formed. The latter is also obtained when RbO_2 is heated *in vacuo* to 600°. The black colour of this oxide shows that it is the intermediate stage between two chief oxidation products (*cf.* p. 748).

The peroxides naturally react as strong oxidising agents in the fused state, and by their aid insoluble metals, alloys, silicates, etc., can be dissolved. They are decomposed by water with formation of H_2O_2 and O_2, thus: $M_2O_4 + 2H_2O \longrightarrow 2MOH + H_2O_2 + O_2$; but Na_2O_2 also gives a hydrate, $Na_2O_2, 8H_2O$. These compounds are very deliquescent in air.

Considerable investigations into the structure of the peroxide ions have been made recently. The alkali "tetroxides," R_2O_4, were believed to contain the ion in

$$\begin{array}{c} :\ddot{O}:^{-} \\ | \\ :\ddot{O}\!\!-\!\!\ddot{O}: \\ | \\ :\ddot{O}:^{-} \end{array}$$

but magnetic susceptibility data suggest the presence of the $O_2{}^-$ ion, containing a three-electron bond and a single bond:

$$\left[:\ddot{O}\!\cdots\!\ddot{O}: \right]^{-}$$

The compound Rb_2O_3 is regarded as $Rb_2O_2 . 2RbO_2$, containing the $O_2{}^-$ ion as above in addition to the peroxide ion $-:\ddot{O}\!\!-\!\!\ddot{O}:^{-}$.

Hydroxides of the Alkali Metals

Formation.—The hydroxides are formed by the addition of water to the oxides M_2O: $M_2O + H_2O \longrightarrow 2MOH$. This mode of preparation is only of practical use in the Li compounds, as the other oxides are not easily obtained. Li_2O dissolves slowly in water, but the other oxides hydrate quickly and with liberation of much heat.

The production of the hydroxides from the metals and water, $2M + 2H_2O \longrightarrow 2MOH + H_2$, is also of no practical value in the preparation of large quantities, because it takes place with such great energy. Potassium, rubidium and caesium catch fire spontaneously on being thrown on to water; sodium ignites only if there is some resistance to its rushing about on the surface. Lithium reacts a little less violently. Small quantities of the hydroxides are obtained (before the evolution of electrochemical methods) by the action of water vapour on the metals—a procedure free from danger. The double decomposition between barium hydroxide and the sulphate of the metal, best at low temperatures $M_2SO_4 + Ba(OH)_2 \longrightarrow 2MOH + BaSO_4$, gives a less pure product, but is useful for the preparation of the hydroxides of Rb and Cs. The cheaper slaked lime may be used in place of $Ba(OH)_2$, thus: $M_2CO_3 + Ca(OH)_2 \longrightarrow 2MOH + CaCO_3$, as originally employed

for causticising sodium carbonate. Both reactions are reversible, and it is not possible to prepare pure solutions of the hydroxides in this way.

The attempt to calculate the equilibrium constant of the reaction $Na_2CO_3 + Ca(OH)_2 \rightleftharpoons 2NaOH + CaCO_3$ on the basis of the known solubility of the lime and chalk in the liquids formed gives results which are not in keeping with those obtained in practice, as the chief reaction is disturbed by several side reactions. For example, the hydrolysis of the dissolved $CaCO_3$ and the formation of insoluble double carbonates of sodium and calcium must be taken into account. Dilution favours the production of hydroxide. Thus, in 2 per cent. solution, 99 per cent. of the soda is causticised, while in 20 per cent. solution only a 91 per cent. yield of the hydroxide is obtained.

The caustic soda obtained in this way is evaporated to crystallisation in iron pans. The product often contains some iron and sodium carbonate unless it has been specially purified. The carbonate remains behind when the hydroxide is dissolved in alcohol, and this method of purification is frequently employed.

These disadvantages do not occur in the electrical process now mostly used for the preparation of the alkali hydroxides. This process depends on the electrolysis of aqueous solutions of the alkali chlorides, when chlorine is obtained at the anode and the alkali metal at the cathode. The alkali metal is then converted by water into the hydroxide, and the hydrogen escapes. It is of course necessary to avoid contact between the chlorine and the alkali hydroxide formed, or they react with formation of hypochlorite. The process is carried out in several ways, of which the diaphragm method, the bell method and the mercury cathode method are the most important.

In the diaphragm method, as used in the Elektron-Fabrik in Griesheim, the anode and cathode space are kept separate by a diaphragm composed of cement or asbestos board. The cement diaphragm is made porous by adding some salt when mixing, the salt being dissolved out later; or the cement is allowed to set in the cold with the addition of very finely powdered ice. All diaphragms are very short-lived; within a month or two, or at the most three months, they are decomposed by the action of the products of electrolysis and must be replaced. The anode, which must not be attacked by chlorine, is best made of Pt-Ir gauze (containing 10 per cent. of Ir), of iron oxide or of artificial graphite. The products of reaction of the latter with chlorine contaminate the escaping chlorine, which is used, for instance, in the manufacture of bleaching powder. The cathodes are made of metals which allow the evolution of hydrogen with the smallest over-voltage (Fe, Ni and sometimes Cu). The electrolysis takes place in a number of cells connected in series, when it is possible to employ a high voltage, although only a few volts are used in each cell. A cell voltage of 3.6-3.7 volts and a temperature of 95° are the usual conditions.

If the current is to be economised the electrolysis must not be taken too far. When the cathode liquid contains 6-7 per cent. KOH (besides 12-15 per cent. KCl) the cell is put out of circuit and the contents evaporated; the alkali chloride crystallises out first and the hydroxide remains in the mother liquor. The hydroxide formed also takes part in conducting the current, and as the OH' ions travel considerably faster than the Cl' ions they take a greater part in the conduction of the current. The electrolysis of the hydroxide serves no

useful purpose and causes the evolution of oxygen at the anode instead of chlorine. The whole problem in the electrolysis of the alkali chlorides is to prevent the transport of current by the hydroxyl ions. The yield of hydroxide from KCl is greater than that from NaCl, owing to the greater mobility of the potassium ions, which move nearly as fast as the chlorine ions, while the sodium ions move much more slowly. The production of potassium hydroxide is thus more efficient than that of sodium hydroxide.

Various devices are used to prevent the dislocation caused by the conduction of the current by hydroxyl ions. If the carbonate is required, CO_2 can be passed into the electrolyte—the CO_3'' ion is less mobile than the OH' ion. The hydroxide can be obtained if a selective diaphragm is used, which permits the Cl' ions to diffuse but confines the OH' ions to the cathode space. These diaphragms have proved of little practical utility, and better results are obtained by the counter-current process of Hargreaves-Bird, in which the electrolyte is made to flow at a rate determined by the rate of production of hydroxide in a direction opposite to that in which the OH' ions tend to migrate. As the hydroxide is removed as fast as it is formed, there is no need for a cathode space, and the iron wire gauze which acts as cathode is closely applied to the diaphragm and the adhering hydroxide removed by a current of steam. In this plant the cathodes are vertical, but in some other arrangements the electrodes are horizontal with the anode above and the cathode below. The processes of Le Sueur, Carmichael and Billiter can only be mentioned here.

The use of the diaphragms is altogether avoided in the bell process, which can be compared to the electrolysis of the alkali chloride in a U-tube, in which the cathode is placed in one limb and the anode in the other. The chlorine given off from the latter is then able to diffuse away without coming into contact with the liquid in the other limb. Mixing is still further discouraged if the U-tube is so placed that the cathode limb is below that which contains the anode, since the hydroxide formed is specifically heavier than the chloride solution, and the chlorine is evolved in the upper limb. In practice the containing tank is the cathode, and in it is suspended a bell with an anode inside it and a pipe at the top to conduct away the chlorine.

In what may be described as the *mercury* methods, the formation of OH' ions in the liquid is prevented altogether. Mercury is used as the cathode, and thus an amalgam of the alkali metal is formed, which is not decomposed by the water, owing to the high over-voltage of hydrogen on a mercury cathode. The amalgam must not, however, be allowed to become too rich in sodium or potassium, or evolution of hydrogen will begin—the limit set is 0·02 per cent. of the alkali metal. The amalgam is then brought into contact with pure water, when it is decomposed with formation of the hydroxide, after which the mercury is returned to the electrolytic cell. The decomposition of the amalgam

is so slow that the process would be impracticable were the rate not increased by making the mercury the anode in the decomposition cell. The actual arrangement is as follows :

> The electrolytic cell is divided into two compartments by a partition which does not quite reach to the bottom ; the layer of mercury on the bottom serves to seal the two compartments, so that the aqueous layer cannot pass from one to the other. One half of the cell is filled with salt solution and the anode placed in it, the other is filled with water and contains the cathode. The mercury thus acts as an intermediate electrode and is the cathode in the brine and the anode in the water. It thus becomes charged with sodium in the brine compartment, and is decomposed by the water in the other half. The cell is given a rocking motion to promote the diffusion of the amalgam (Castner-Kellner process). In a more recent type of plant, the mercury flows over a sloping floor in the brine cell, passes over a weir into a separate cell below, where the amalgam is decomposed. The mercury is returned to the brine cell by an Archimedean screw.

Properties.—The alkali hydroxides are all white, and crystallise from the fused state in opaque brittle crystals which form radially from nuclei. They fuse readily at a red heat, particularly if the melting point is lowered by the addition of a little water. With the exception of lithium hydroxide (p. 412) they do not lose water even at very high temperatures but vaporise unchanged, the temperature of volatilisation being lower as the atomic weight of the metal becomes greater. Rubidium hydroxide is completely volatile at the temperature of the Bunsen flame. The *densities* of the solid hydroxides are :

NaOH	KOH	RbOH	CsOH
2·130	2·044	3·203	4·018

The alkali hydroxides are very hygroscopic—that of lithium less so than the others. They dissolve in water with great evolution of heat and are very strong bases.

Numerous crystalline hydrates of these hydroxides are known. LiOH crystallises with 1 mol. H_2O; hydrates of NaOH containing 7, 5, 4, 3·5, 2 and 1 mol. H_2O are known, the last three being stable at room temperature; KOH forms hydrates with 4, 2 and 1 H_2O. The change from tetra- to di-hydrate takes place at $-33°$, that from di- to monohydrate at $32·5°$. Both the latter hydrates can thus be obtained in the evaporation of solutions of caustic potash, and it is found that the dihydrate separates from solutions containing less than 58 per cent. KOH, the monohydrate from solutions containing between 58 and 85 per cent., and more concentrated solutions give the anhydrous hydroxide.

The solubility of the alkali hydroxides is very pronounced. Lithium hydroxide, in analogy with the calcium compound, is not very soluble in water (11 per cent. at 10°; 13 per cent. at 75°); it is also only slightly soluble in alcohol, in which the other hydroxides of this group

are easily soluble. The following solubilities are given without reference to the hydrate which forms the solid phase :

100 g. water dissolve at		0°	50°	125°	
		97	140	213 g. KOH,	
and at	0°	10°	20°	50°	80°	192°
	42	51	109	145	313	521 g. NaOH.

In order to find the percentage of alkali in a solution, it is useful to remember that the figures in the first two decimal places in the sp. gr. of the latter approximate to the percentage of alkali hydroxide in the solution :—

Sp. gr.	.	.	.	1·05	1·092	1·188	1·290	1·399	1·514
Per cent. KOH .	.	.		5	10	20	30	40	50
Sp. gr.	.	.	.	1·055	1·111	1·222	1·331	1·434	1·530
Per cent. NaOH	.	.		5	10	20	30	40	50

Fused alkalis attack many metals, e.g. platinum, so that caustic alkalis cannot be melted with impunity in vessels of platinum. The action is due to the formation of small quantities of the free alkali oxide which combines with the oxygen of the air to give a peroxide, causing the oxidation of the metal. The metal is not attacked if air is not admitted. Metals like platinum, which have acidic oxides, are particularly prone to this etching by alkalis, for the consequent formation of salts increases the rate of attack. The alkali hydroxides are used as oxygen carriers in the fused state in some organic oxidations.

The peroxide hydrates of the alkali metals include two groups of compounds—the addition products of water or hydrogen peroxide to the peroxides or hydroxides, and the salts of ozonic acid.

The following compounds of the first class have been described :

$$Li_2O_2,H_2O_2,3H_2O \qquad K_2O_2,2H_2O_2$$
$$Na_2O_2,8H_2O \qquad Na_2O_2,2H_2O_2,4H_2O \qquad NaO_2H.$$
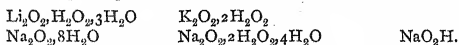
The last of these, sodyl hydroxide, may be regarded as an acid salt of H_2O_2; it is obtained by shaking Na_2O_2 with alcohol: $Na_2O_2 + C_2H_5OH \longrightarrow NaO_2H + C_2H_5ONa$. It is a white powder with a great tendency to give up oxygen, so much so that flame is produced when it decomposes spontaneously.

The other hydrated peroxides are formed when the peroxides are dissolved in water or when hydrogen peroxide is added to solutions of the hydroxides and the solutions cooled, allowed to evaporate or precipitated by alcohol. They form white crystalline powders and can be dehydrated in the exsiccator without loss of H_2O_2; they may be compared with the analogous compounds of the alkaline earths (p. 423). On decomposition by heat they give orange-coloured intermediate products which are probably similar to CaO_4 (p. 421).

The so-called ozonates are now more properly called *oxyhydroxides* and have a general formula $2MOH,O_2$ or something similar ; they are formed when ozone is passed over the solid hydroxides of potassium, rubidium and caesium. The white solids turn orange, but the reaction

is probably only superficial, for KOH only fixes 8 per cent., RbOH 4.9 per cent. and CsOH 2.2 per cent. of oxygen, the whole of which is given off as inactive oxygen and not as ozone when the fresh compound is wetted. No H_2O_2 is formed on solution, a distinction between this and the preceding class of compound. On keeping, the colour disappears, and only the yellow colour of the peroxide remains; further, the aged substance gives H_2O_2 on treatment with water, so that the oxyhydroxides are gradually converted into peroxide hydrates.

Oxides of the Metals of the Alkaline Earths

Three types of oxide are known with certainty in the alkaline earths:

I. MO (white)	BaO	SrO	CaO	MgO	BeO
II. MO_2 (white)	BaO_2	SrO_2	CaO_2	...	...
III. MO_4 (brown)	BaO_4	(SrO_4)	CaO_4	...	...

Only the hydrated form of MgO_2 is known. Black suboxides of the general formula M_2O have been described for barium and magnesium, but it is doubtful whether they are definite compounds.

The Monoxides, MO.—These oxides are formed when the hydroxides, carbonates or nitrates are decomposed by heat, the stability of these compounds being roughly parallel to the strength of the oxides as bases; and whereas the hydroxides or carbonates of the alkalis cannot be appreciably decomposed by heating, those of this group are all decomposed at high temperatures (for the dissociation temperatures of the carbonates see p. 798). The nitrates of the alkalis are decomposed to nitrites on heating, while those of the heavy metals give oxides without the nitrite stage; but at moderate temperatures the nitrates of the alkaline earths give a mixture of oxide and nitrite, with complete decomposition to oxide at very high temperatures. Barium is nearest to the alkalis in this property—its carbonate is the most difficult to decompose — while magnesium (and Be) is most unlike them of the metals in this group. As has already been seen with lithium, the lightest member of the group approaches the elements of the next group of the periodic system in its properties.

The hydrolysis of the salts of these metals is also intermediate between the very slight tendency of those of the alkalis and the pronounced habit of the heavier metals. Their salts with strong acids are not hydrolysed, or only to a slight extent, in aqueous solution, but if heated in a current of steam the acid is removed and the oxide remains. This reaction is most rapid with the metals of low basic power, and is employed on the large scale for the production of magnesium oxide and hydrochloric acid from the magnesium chloride, which is a valueless by-product from the potash industry.

The method of production mostly used is that which involves the

decomposition of the carbonates, but owing to the high temperature of decomposition of barium carbonate the hydroxide is usually employed. A temperature of 812° is enough to cause the decomposition of calcium carbonate, and the dissociation even occurs at lower temperatures if the carbon dioxide is removed from the equilibrium mixture, *e.g.* by a current of air, which is the method used in lime kilns. The lime formed at lower temperatures has the further advantage of being readily slaked to the hydroxide, but when calcined at a high temperature it is "over-burnt" and slakes very slowly. The rate of solution of the lime in acids is also diminished by this treatment, though the total thermal effect remains the same. Ignited BeO, like alumina, is insoluble in acids, with the exception of concentrated sulphuric acid.

The oxides are crystalline when prepared at a high temperature, but as ordinarily manufactured they form loose powdery masses. Magnesia made from the carbonate is a very light powder. The oxides assume the crystalline form of cubes at temperatures below their melting points, as they have even then a considerable vapour pressure. Beryllium oxide is exceptional in giving hexagonal crystals, and the cubic form is not the stable form of the other oxides, as the cubes break up into doubly refracting crystals after a time.

The densities of the oxides are as follows :

BeO	MgO	CaO	SrO	BaO
3·18	3·56	3·40	4·75	5·72

These densities refer to the crystalline oxides ; the amorphous oxides have densities which are less than these and which depend on the previous history of the sample.

The cubic crystals of these oxides have a structure similar to that of rock salt (p. 299). The lengths of the sides of the unit cubes are :—

BeO	MgO	CaO	SrO	BaO
3·796 (?)	4·20	4·76	5·10	5·50 Å

These oxides are very difficult to melt but are liquefied in the electric arc. Their refractoriness, combined with their inertness to many reagents after they have been ignited, makes them useful in the construction of furnace linings, etc. The boiling point of MgO is about 2800°, that of CaO about 2850°.

Luminosity.—When strongly heated, these oxides emit a brilliant light. The bright flame of burning magnesium is due to the MgO in it, and the oxide shines just as brightly if heated by other means to the same temperature. The intensity is not therefore due to the combustion but to the same cause as that of the incandescent mantle (see below). Drummond's limelight is obtained when a stick of lime is heated in an oxyhydrogen flame. The light emitted by a piece of zirconia is even more brilliant.

The cause of the luminosity has been most carefully studied from the point of view of the incandescent gas mantle (Auer von Welsbach), which is composed of 99 per

cent. thoria and 1 per cent. ceria, with traces of BeO, Al_2O_3, etc., to make it more robust. The light is not a mere luminescence phenomenon, nor is it due to the temperature of the flame, for if the ceria is omitted the gas burns at the surface of the thoria but the light is much less intense. The total energy liberated is the same whether the ceria is there or not, but the luminosity is diminished just as much by excess of ceria as by a deficiency. The actual temperature of the mantle is, moreover, lower than that of the flame, and it glows just as well if it is heated by a stream of hot gases which do not burn around it. There is thus no question of a catalytic combustion at the surface giving a local high temperature,[1] but rather a selective radiation of light of visible wave-length. A pure thoria mantle radiates scarcely any visible light, but the addition of the small quantity of ceria shifts the bulk of the radiation from the infra-red to the visible part of the spectrum. The radiation from pure ceria is also mainly in the infra-red region, so that excess of ceria in the mantle causes a decrease in the luminosity. Other oxides, such as those of chromium, manganese, uranium and platinum, affect the thoria in the same way as CeO_2; some give mantles which emit an even better light, but none possess the durability of the thoria-ceria mantle.

The Peroxides, MO_2.—The formation of stable peroxides at high temperatures is characteristic of the more electropositive metals. The property is not very pronounced in lithium and is entirely absent in beryllium, while of the alkaline earths, barium forms a peroxide most readily in the dry way. Magnesium peroxide exists only in the form of a hydrate (*cf.* p. 423), and although calcium peroxide is formed as a stable powder by dehydrating its hydrate, it cannot be formed from lime and oxygen even at a pressure of 190 atm. The peroxide formed by dehydration is stable to above 200°. SrO_2 can be prepared synthetically from SrO and oxygen at 400°, and a pressure of 90 atm.[2] and BaO_2 is easily made by this method even from the oxygen of the air.

The formation of barium peroxide takes place in the reversible reaction $2BaO + O_2 \rightleftharpoons 2BaO_2$ when a little water vapour is present. The dissociation pressure varies with temperature as follows:

Temperature	525°	670°	735°	775°	790°
Dissoc. press.	20	80	260	510	670 mm.

The peroxide is thus formed from atmospheric oxygen (0·2 atm. pressure) at 700° but is decomposed at higher temperatures. This property was used for a considerable time as a method of obtaining oxygen from the air (Brin's process), the oxide being subjected to alternate high and low temperature or pressure. Success in the operation depended on the preservation of the oxide in a porous state— made difficult by the fact that BaO_2 melts at a lower temperature than BaO—and the exclusion of carbon dioxide. Barium peroxide is a white powder like magnesia; it is naturally a powerful oxidising agent when heated dry with many substances, and in water it gives a mixture of barium hydroxide and hydrogen peroxide, and is largely employed

[1] Le Chatelier and Boudouard, *Compt. rend.*, 1898, 126, 1861.
[2] Fischer and Plötze, *Z. anorg. Chem.*, 1912, 75, 30.

for the manufacture of this substance (p. 406). The hydrates of BaO_2 are discussed on p. 423.

The Peroxides, MO_4.—The peroxide hydrates, *e.g.* BaO_2, H_2O_2, are yellow in colour but soon lose this appearance. The coloured compounds are best made by the action of warm 30 per cent. H_2O_2 on the hydrated dioxides—the calcium compound is the most stable, but the barium compound has not yet been isolated. The yellow product from calcium peroxide is dehydrated at 130°, but can be heated to 270° without losing colour. Traube and Schultz[1] found that the yellow compounds gave only ordinary oxygen when treated with water, but after they had become white H_2O_2 was formed. They are thus comparable to the alkali tetroxides (p. 412). The product from calcium contains only 8·7 per cent. of CaO_4, the rest being ordinary peroxide, and the less stable barium tetroxide, formed by the interaction of H_2O_2 and BaO_2, decomposes at 50°-60° and contains even less of the pure tetroxide. The low yield is probably due to the decomposing action of the water present during formation. The action of ultra-violet light on the peroxide hydrates gives brown products at the ordinary temperature. An oxide of formula BaO_3 has also been described.

The Hydroxides.—*Hydroxides of the Formula* $M(OH)_2$.—These hydroxides are formed by the precipitation of solutions of the salts of the alkaline earths with reagents containing hydroxyl ions, or by the action of water on the oxides. They are all precipitated by NaOH or KOH at suitable concentrations, but ammonia precipitates only the less soluble—magnesium and beryllium hydroxides. The former is only partly precipitated, as the concentration of OH ions in aqueous ammonia is too low to complete the reaction : $MgCl_2 + 2NH_4OH \longrightarrow Mg(OH)_2 + 2NH_4Cl$. The tendency of the ammonium hydroxide to remain in the molecular condition is increased by the presence of the $NH_4^{\cdot}$ ions formed in the reaction, so that the solubility product $\dfrac{Mg^{\cdot\cdot} \times (OH)'^2}{Mg(OH)_2} = K$ is not exceeded owing to lack of OH' ions, the concentration of which is maintained by the solution of some of the precipitate. If ammonium salts are already present in the solution the addition of ammonia gives no precipitate of the hydroxide ; complex ion formation by the Mg may also contribute to its non-precipitation under these conditions.

The quantity of heat liberated when the oxides combine with water increases with rising atomic weight of the alkaline earth metals. There is no noticeable evolution of heat with BeO, but when MgO is wetted the mixture becomes warm, especially if the MgO has been made by ignition of the carbonate at low temperature—the oxide obtained from the nitrate is less reactive, as a red heat is necessary to decompose that salt.

[1] *Ber.*, 1921, **54**, 1626.

Moderately ignited MgO combines slowly with water and sets like a hydraulic cement to a hard mass resembling marble. After prolonged ignition at a white heat the MgO is dead burnt and cannot be hydrated. Lime can also be overburnt in the same way; but when produced at a moderate temperature it hydrates readily, with an evolution of heat greater than that given by magnesia. On the addition of water combination ensues, with hissing and escape of steam, and the slaked lime crumbles to a fine white powder. The rate of slaking is much reduced by the presence of impurities in the lime or in the water.

The energy of hydration increases in passing to SrO and BaO. The hydroxides are white powders of density:

$$Ba(OH)_2 : 4\cdot49 \qquad Sr(OH)_2 : 3\cdot62 \qquad Ca(OH)_2 : 2\cdot24.$$
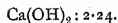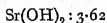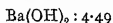
The dehydration of the hydroxides is most easily carried out when the heat of formation is low. $Mg(OH)_2$ loses its water above 100°, $Ca(OH)_2$ has a dissociation pressure of 760 mm. at 450°, but $Sr(OH)_2$ does not give this pressure even at 700°.

The more insoluble oxides of Be and Mg are precipitated from solution in the amorphous state, while the more soluble form crystals. $Be(OH)_2$ forms a jelly which is similar to $Al(OH)_3$ in its lack of constant water content and in its alteration of properties on ageing (cf. p. 454). $Mg(OH)_2$ appears as a slimy flocculent precipitate; in these hydroxides the determination of the water content gives indefinite and variable results. The crystalline hydroxides of Ba and Sr have, on the other hand, definite hydrates: $Ba(OH)_2$, 1 and $8H_2O$; $Sr(OH)_2$, 1 and $8H_2O$. The octahydrate is the common form of the hydroxides of Ba and Sr, and forms fairly large clear crystals, but hydrates of calcium hydroxide, $Ca(OH)_2 . \frac{1}{2}H_2O$ and $Ca(OH)_2 . H_2O$, are very unstable. The solubilities of the higher hydrates rise with temperature, but that of the anhydrous hydroxides is less at high temperatures; hence the solubility of calcium hydroxide is less in hot water than in cold, but the solubilities of barium and strontium hydroxides increase with rise in temperature. 100 parts of the saturated solutions contain:

	0°	30°	50°	70°	80°
Parts BaO	1·5	5·0	11·75	31·9	90·77
	0°	50°	75°	90°	100°
Parts SrO	0·35	2·13	5·29	11·95	19·34

and one part of CaO is dissolved by

	776	962	1330	1482	parts of water.
at	15°	40°	70°	80°	

The solubility of magnesium hydroxide is $3\cdot5 \times 10^{-4}$ mole per litre at 10° and $2\cdot3 \times 10^{-4}$ mole at 29°.

In general, the solubility of the hydroxides becomes less as the series is traversed from Ba to Mg; the recorded solubility of $Be(OH)_2$ is

probably the content of the colloidal solution, and its true solubility is probably fifty to a hundred times smaller than that of $Mg(OH)_2$. (*Cf.* the table on p. 450.) Barium and strontium hydroxides, but not calcium hydroxide, can be crystallised from water. The rapid increase of the solubility of barium hydroxide with rise of temperature is very remarkable. The hydroxides dissolve with evolution of heat owing to the simultaneous formation of their hydrates, but the hydrates themselves dissolve with absorption of heat. The barium compound melts at 80° in its water of crystallisation and then has a dissociation pressure of 250 mm.; that of strontium is dehydrated at 100° while the monohydrate of calcium hydroxide is decomposed at 70°.

The most important chemical property of these hydroxides is that of acting as strong bases; on this account, $Ba(OH)_2$ is much used in the laboratory, while slaked lime is largely employed in industrial processes.

The Peroxide Hydrates.—The peroxide hydrates of the alkaline earths are formed from the hydroxides of the metals and hydrogen peroxide, or by the addition of Na_2O_2 to solutions of the salts of the metals, or by precipitation of solutions of the salts containing H_2O_2 with ammonia.[1] There are two distinct types in these compounds.

1. Hydrated peroxides, MO_2, xH_2O, which usually contain eight mols. of water. They form pearly scales which lose their water without decomposition if carefully heated and which are rather more soluble than the hydroxides of the metals.

2. Compounds of the peroxides with hydrogen peroxide, MO_2, xH_2O_2, which mostly have two mols. of H_2O_2, though a barium compound containing one mol. is also known. They are formed in the cold when concentrated H_2O_2 is used. At higher temperatures the peroxides are obtained free from both water and hydrogen peroxide. The decomposition of the peroxides on heating is further dealt with in relation to the oxides MO_4 on p. 421.

The corresponding beryllium compounds have not been obtained, and those of magnesium are only known in an impure state; among the other metals cadmium, zinc and copper give similar compounds (p. 460).

The Rare Earths

As the oxides of the rare earths are among their most important compounds, a general discussion of their separation and properties is introduced at this point.

Compounds of elements which are not isotopic (p. 77) can usually be separated from one another in one or at least in a few operations. In the group of rare earths, however, the properties of the elements are for the most part so extraordinarily similar that their separation from each other offers quite unusual difficulties. The differences between

[1] Riesenfeld and Nottebohm, *Z. anorg. Chem.*, 1914, 89, 405.

the individual elements (with the exception of cerium) are only gradual, somewhat similar to those between the members of the homologous series of organic chemistry. This difficulty of separation pervades the chemistry of the rare earths, and in the evolution of the methods of separation their analytical chemistry was the main work of the chemists who investigated these elements.

The discussion of the rare earths which follows will be restricted to the following elements, all of which properly fall in the third group of the periodic system, but have the following atomic numbers:

21	39	57	58	59	60	61	62
Sc	Y	La	Ce	Pr	Nd	Il	Sa

63	64	65	66	67	68	69	70	71
Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu (Cp)

Thorium is also often included with the rare earth metals, since it has many properties in common with them, especially with quadrivalent cerium, and occurs in nature associated with its homologues, titanium and zirconium. It is remarkable that niobium and tantalum, as well as uranium and tungsten, are often present in the rare earth minerals, though their chemistry is essentially different.

The existence of scandium was predicted by Mendeléev from the periodic system. It is the element which he designated "Ekaboron," and is placed below aluminium in the system. Yttrium, again, occurs below scandium, but the other rare earths come in a lower series in the system; for a discussion of their position cf. p. 30.

The great similarity in the properties of the rare earths is due to the entry of the additional electrons, consequent on increasing atomic number, into the *inner* layers of the electron shell, instead of the outer layer only being built up.[1] This is shown in the table on p. 6. The "valency-electrons" which remain in the outer levels (5_8 and 6_1) are the same for all the rare earths. The increase in positive charge on the nucleus with rising atomic number is equalised by accretion of electrons in the hitherto partially occupied 4_4 level. The addition of electrons at this depth has little effect on the chemical properties of the atom, for the valency is unaltered by their presence and they take no part in compound formation. The interruption of the building-up of the outer shells from lanthanum to lutecium results in the occupation of one square only in the periodic system by these elements, as that system registers increases in the number of electrons in the outer layers.

The Lanthanide Contraction.—The consideration of the structure of the atoms of the rare earths has been of great importance in the increase of our knowledge of the connection between atomic structure and the properties of the elements. The work of von Hevesy[2] and of V. M. Goldschmidt[3] on the lanthanide contraction and its effects may

[1] Cf. Bohr, *Nature*, 1921, 107, 104.
[2] Z. anorg. Chem., 1925, 147, 217.
[3] Geochemische Verteilungsgesetze, Oslo, 1925.

be quoted as an example. The elements, Sc, Y, La, lie in the same group of the system but in consecutive long series. Each has three valency electrons; but while the total charge on the nucleus remains equal throughout to the total number of electrons, these three valency electrons are in a higher energy level in yttrium than in scandium, while in lanthanum they are still further from the nucleus. Consequently the action of the nucleus on the valency electrons becomes continuously less in the series Sc—Y—La, as also, for instance, in the three elements K—Rb—Cs. The electropositive character of the atom is thereby increased, and the valency electron of Cs is readily given up, as it is so far from the nucleus and is so heavily screened by the inner layers of electrons. In general, one may say that in the groups of the periodic system the action of the nucleus on the valency electrons diminishes with increasing atomic number.

On the other hand, in the series from lanthanum through cerium and praseodymium to lutecium, the conditions are different; with increasing atomic number the valency electrons become more and more firmly held by the nucleus. These electrons are not pushed further away from the nucleus but remain in the same level, with an ever-increasing charge on the nucleus as the atomic number becomes greater. Hence the force exerted on them becomes steadily larger, for although the entry of more electrons into the inner levels has a greater screening effect, this does not compensate for the closeness and increased charge of the nucleus.

The determination of densities actually shows an increase in atomic volume in the series Sc—Y—La, and a decrease in the series La—Ce . . . Lu. Indeed, so great is the latter that between dysprosium and holmium the value for yttrium is reached again, though that of scandium lies beyond luteceium. This effect is very apparent from the measurement of the side of the unit cube in the crystals of the oxides of these elements by the X-ray method.[1] Each cube contains 16 molecules of R_2O_3.

At. No.	21	39	57	58	59	60	62	63	64	65	66	67
	Sc	Y	La	Ce	Pr	Nd	Sa	Eu	Gd	Tb	Dy	Ho
a in cm. $\times 10^{-8}$	9.79	10.60	11.4	11.15	11.11	11.05	10.89	10.84	10.79	10.69	10.62	10.58

At. No.	68	69	70	71
	Er	Tm	Yb	Lu
a in cm. $\times 10^{-8}$	10.50	10.45	10.40	10.37

In a similar way the molecular volumes of the octahydrates of the sulphates show a steady decrease from lanthanum to luteceium; that of the yttrium compound falls in the middle of the series—next to gadolinium.

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volume being less the electrons are more strongly held. It also follows that in the separation of the earths yttrium always remains near holmium, to which it is closest in volume, and scandium lies outside the sequence of the lanthanides beyond lutecium.

The lanthanide contraction is important for elements which do not belong to the rare earth group. Normally there is a regular periodicity in atomic volume of such a kind that elements of the later series always have a greater atomic volume than the corresponding elements in the earlier series. This contraction in the lanthanum series, however, breaks the sequence and even reverses the effect, so that in the same group there is a diminution in the atomic volume for increasing atomic number. Consequently, the elements which follow lanthanum show a much smaller increase in the atomic volume than would obtain if the disturbing effect of the building-up of the inner layers was absent. Hafnium, for instance, which falls under zirconium in the fourth group, is not very different in atomic volume, and as both elements also have the same number of valency electrons the great chemical similarity of the two elements is explained.

Thus the differences between corresponding elements are greater before the lanthanide series than after. This can be exemplified by the dimensions of the crystal lattices, which have been collected by Goldschmidt.

CRYSTAL LATTICE DIMENSIONS IN CM. × 10⁻⁸

Entirely Before the Lanthanide Series

	Ti	Zr	Ce	Ca	Sr	Ba
a.	2·97	3·23	3·65	4·760	5·104	5·496

		a		a		a
Before Lanthanide Series .	. ⎧Cu, 3·615	Ni, 3·53	Cr, 2·895
" " .	. ⎨Ag, 4·076	Pd, 3·873	Mo, 3·143
After Lanthanide Series .	. ⎩Au, 4·08	Pt, 3·903	W, 3·150

Classification.—If the rare earths are grouped according to their similarity they may be divided with advantage into three sub-groups, which, however, still bear a considerable resemblance to each other. These three groups are: 1, the cerium earths; 2, the terbium earths; 3, the ytterbium earths. The following table gives the atomic weights of the individual elements and the colour of the tervalent salts and oxides except where otherwise indicated.

CERIUM EARTHS

		At. Wt.	Colour of Salts.	Colour of Oxides.
La	Lanthanum	138·92	colourless	...
Ce	Cerium	140·13	colourless	Ce^{iii} unknown
			Ce^{iv} yellow to red	Ce^{iv} quite pale yellow
Pr	Praseodymium	140·92	leek green	yellowish green
Nd	Neodymium	144·27	rose to violet red	bluish grey
Il	Illinium	...	yellow	...
Sa	Samarium	150·43	pale yellow	almost white
			Sa^{ii} orange yellow	

TERBIUM EARTHS

Eu	Europium	152·0	pale pink	nearly white
			Eu^{II} colourless	
Gd	Gadolinium	156·9	colourless	white
Tb	Terbium	159·2	colourless	white

YTTERBIUM EARTHS

Dy	Dysprosium	162·46	yellow	white
Ho	Holmium	163·5	yellow	yellow
Er	Erbium	167·64	pink	pink
Tm	Thulium	169·4	green	greenish white
			Tm^{II} brick red	
Y	Yttrium	88·92		
Yb	(Neo-) Ytterbium	173·04	Yb^{II} green	white
Sc	Scandium	45·10	colourless	
Lu	Lutecium (Cassiopeium)	175·0		

In general this grouping follows the atomic weights, but scandium and yttrium, with atomic weights much lower than those of the other earths, are in the last group owing to the lanthanide contraction.

There is much evidence that the extent of the chemical similarity between the separate rare earths is intimately connected with the dimensions of the crystal lattices. The sequence obtained in fractionation is parallel to that of the sizes of the lattice units and in the pairs of elements which show the greatest chemical similarity (Sa—Eu; Er—Tm; Yb—Lu) the crystal dimensions are also almost identical, as may be seen, for example, in the table of the oxide dimensions on p. 425.

The subdivision of the "lanthanide" group into two sub-groups— La to Gd and Gd to Lu—appears to be justified from the structure of the atoms; there is general similarity between an element in this series and the one eight places away from it. They occupy, for example, corresponding positions on the magnetic susceptibility curve. There is maximum paramagnetism in the middle of these two groups, the end members being diamagnetic. The paramagnetism reaches a maximum with Dy_2O_3 which is about twelve times more strongly paramagnetic than Fe_2O_3. As paramagnetism is due to the building-up of incomplete inner levels of electrons (p. 48) it would appear that the 14 extra electrons inserted in the rare earths enter in two levels, the first being filled up at about Gd and the second at Lu. The colours of the compounds are in agreement with this suggestion, as paramagnetic compounds are usually coloured, both properties being signs of incomplete electron shells. The first, midmost, and last member of the rare earths form colourless compounds (La, Gd, Lu).

Determinations of atomic volume give a main curve in two parts, La—Nd, Gd—Lu, the position of Sa being uncertain, with Eu and Yb lying off the main curves. The latter have much larger atomic volumes corresponding with their tendency to form bivalent compounds. The

volume being less the electrons are more strongly held.   It also follows
that in the separation of the earths yttrium always remains near
holmium, to which it is closest in volume, and scandium lies outside
the sequence of the lanthanides beyond lutecium.

The lanthanide contraction is important for elements which do not
belong to the rare earth group.   Normally there is a regular periodicity
in atomic volume of such a kind that elements of the later series always
have a greater atomic volume than the corresponding elements in the
earlier series.   This contraction in the lanthanum series, however,
breaks the sequence and even reverses the effect, so that in the same
group there is a diminution in the atomic volume for increasing atomic
number.   Consequently, the elements which follow lanthanum show
a much smaller increase in the atomic volume than would obtain if
the disturbing effect of the building-up of the inner layers was absent.
Hafnium, for instance, which falls under zirconium in the fourth group,
is not very different in atomic volume, and as both elements also have
the same number of valency electrons the great chemical similarity of
the two elements is explained.

Thus the differences between corresponding elements are greater
before the lanthanide series than after.   This can be exemplified by
the dimensions of the crystal lattices, which have been collected by
Goldschmidt.

CRYSTAL LATTICE DIMENSIONS IN CM. $\times 10^{-8}$

Entirely Before the Lanthanide Series

	Ti	Zr	Ce	Ca	Sr	Ba
a.	2·97	3·23	3·65	4·760	5·104	5·496

		a	a	a
Before Lanthanide Series .	. Cu, 3·615	Ni, 3·53	Cr, 2·895
„ „	.	Ag, 4·076	Pd, 3·873	Mo, 3·143
After Lanthanide Series .	. Au, 4·08	Pt, 3·903	W, 3·150

Classification.—If the rare earths are grouped according to their
similarity they may be divided with advantage into three sub-groups,
which, however, still bear a considerable resemblance to each other.
These three groups are: 1, the cerium earths; 2, the terbium earths;
3, the ytterbium earths.   The following table gives the atomic weights
of the individual elements and the colour of the tervalent salts and
oxides except where otherwise indicated.

CERIUM EARTHS

		At. Wt.	Colour of Salts.	Colour of Oxides.
La	Lanthanum	138·92	colourless	...
Ce	Cerium	140·13	colourless	Ce^{iii} unknown
			Ce^{iv} yellow to red	Ce^{iv} quite pale yellow
Pr	Praseodymium	140·92	leek green	yellowish green
Nd	Neodymium	144·27	rose to violet red	bluish grey
Il	Illinium	...	yellow	...
Sa	Samarium	150·43	pale yellow	almost white
			Sa^{ii} orange yellow	

TERBIUM EARTHS

Eu	Europium	152·0	pale pink	nearly white
			Eu^{II} colourless .	
Gd	Gadolinium	156·9	colourless	white
Tb	Terbium	159·2	colourless	white

YTTERBIUM EARTHS

Dy	Dysprosium	162·46	yellow	white
Ho	Holmium	163·5	yellow	yellow
Er	Erbium	167·64	pink	pink
Tm	Thulium	169·4	green	greenish white
			Tm^{II} brick red	
Y	Yttrium	88·92		
Yb	(Neo-) Ytterbium	173·04	Yb^{II} green	white
Sc	Scandium	45·10	colourless	
Lu	Lutecium (Cassiopeium)	175·0		

In general this grouping follows the atomic weights, but scandium and yttrium, with atomic weights much lower than those of the other earths, are in the last group owing to the lanthanide contraction.

There is much evidence that the extent of the chemical similarity between the separate rare earths is intimately connected with the dimensions of the crystal lattices. The sequence obtained in fractionation is parallel to that of the sizes of the lattice units and in the pairs of elements which show the greatest chemical similarity (Sa—Eu; Er—Tm; Yb—Lu) the crystal dimensions are also almost identical, as may be seen, for example, in the table of the oxide dimensions on p. 425.

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Determinations of atomic volume give a main curve in two parts, La—Nd, Gd—Lu, the position of Sa being uncertain, with Eu and Yb lying off the main curves. The latter have much larger atomic volumes corresponding with their tendency to form bivalent compounds. The

atomic volumes of Ce, Pr, and Tb, which forms quadrivalent compounds all lie below the main curves. These features correspond with the measurements of magnetic susceptibilities.[1]

All the metals of the rare earths are tervalent, but samarium, europium and ytterbium are also bivalent and there is evidence for bivalency in La, Gd, Tm and Lu. Cerium forms very stable quadrivalent compounds besides the ordinary tervalent ones. In the cerium atom there is one electron in the 4_4 level, which is so weakly retained that it is lost, together with the three valency electrons, to give an ion of valency 4. In praseodymium, neodymium and terbium intermediate stages only are reached, e.g. the highest oxide of Pr is Pr_6O_{11}. Only cerium forms quadrivalent salts and these show a more or less pronounced tendency to revert to the tervalent condition particularly in solution. The double salts are more stable and the apparently simple ones probably also have a complex structure.[2]

These relations are similar to those of the compounds of nickel and cobalt; praseodymium is comparable to nickel, of which the oxide of higher valency is quite stable, though the salts correspond only to the lower valency. Cerium may be compared with cobalt, with an even more stable higher oxide which is easily transformed into salts of lower valency on solution in acids, while the complex cobalt compounds of higher valency are quite stable. Just as CoO is further oxidised on heating in the air, Ce_2O_3 is converted into CeO_2 by this treatment. In the quadrivalent condition cerium naturally has quite different properties from those of the tervalent, and in the former state differs considerably from the rest of the elements of the rare earths, which are normally tervalent, and thus oxidation serves to separate it from the others (cf. p. 438).

In their compounds the rare earths do not resemble the tervalent elements but are more closely related in their behaviour to the bivalent alkaline earths, and the most strongly basic, such as lanthanum (cerium group), are like calcium in many ways. Those in the ytterbium group are less basic and have a closer resemblance to aluminium. The strong basicity of the group containing lanthanum is shown by the fact that, like the alkaline earth salts, their salts are not hydrolysed in solution. Their oxides take up carbon dioxide from the air and also form the hydroxide so readily that they hiss like lime when water is poured on to them. Even after being heated to redness they dissolve in acids, like the oxides of the alkaline earths, and unlike the oxides of iron, aluminium and chromium. The oxide of quadrivalent cerium, on the other hand, resembles the oxides of these three metals, for it is insoluble in acids after ignition. It is so much less basic than the tervalent oxides that it acts as an acid towards them, and forms coloured salts, especially with the strongest bases of this group (La_2O_3, Pr_2O_3). While cerium dioxide is only very pale yellow, it becomes deep brown

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as a result of this salt formation, when small quantities of these trioxides or of Ce_2O_3 are mixed with it. These trioxides also become insoluble if they contain an appreciable quantity of cerium dioxide; they are then no longer present as such, but as salts of the acid $Ce(OH)_4$. This brown coloration is therefore a sharp criterion of the purity of cerium dioxide.

It is also very remarkable that praseodymium and neodymium are induced by the presence of cerium to form (brown) oxides, approaching in composition to PrO_2 and NdO_2, on calcination in air, while addition of lanthanum hinders this conversion.

Oxides and Hydroxides.—The oxides, which are usually employed for the separation of the earths from each other, are obtained by heating the hydroxides, nitrates, oxalates, or, with more difficulty, the sulphates. Their properties may vary greatly, according to the method of preparation; when made from the oxalates, the method which requires the lowest temperature, they are most reactive. Like thorium dioxide (p. 819), cerium dioxide gives colloidal solutions if it has been obtained in a spongy form; from these solutions it may be precipitated as a gel. The oxide of tervalent cerium is not readily made, as it is converted into CeO_2. The resemblance to thorium, zirconium, etc., is also shown by the formation of peroxides such as $La(OH)_3 . OOH$ and the orange $Ce(OH)_3 . OOH$ when hydrogen peroxide is added to the precipitated hydroxides in alkaline solution (*cf.* p. 843).[1]

The heat of formation of the oxides of the rare earths is particularly high; no metals have a higher affinity for oxygen (*cf.* the list on p. 441). This is especially notable in the ytterbium earths. The " Mischmetall " of commerce, an unseparated reduction product from a natural mixture of rare earths, is a better reducing agent than aluminium. It is therefore of great value in the Goldschmidt process. In the following list the heats of formation of the oxides from the metal and oxygen per equivalent are given. The equivalent number for " Mischmetall " refers to a metal containing 40 per cent. cerium, in which the cerium is assumed to be converted to CeO_2 :

$\frac{1}{6}$ Al_2O_3	$\frac{1}{6}$ Pr_2O_3	$\frac{1}{2}$ MgO	$\frac{1}{6}$ Nd_2O_3	$\frac{1}{6}$ La_2O_3	$\frac{1}{6\cdot8}$ " Mischmetall "
64·3	68·7	71·5	72·5	74·1	78.8 Cal.

The heat of oxidation is not parallel to the basicity of the oxide formed (*cf.* below). The oxides are naturally difficult to reduce because of the great heat of formation, and the metals can be obtained only by electrolysis of fused salts.

The tervalent oxides of these elements exist in several different forms, and the ranges of stability show interesting relations to one another. The transition temperatures are shifted regularly with increasing atomic number. Of the three types of sesquioxide met with

[1] For the interesting cerium percarbonate see p. 395.

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only type C can be obtained from holmium onwards, as the transition temperatures of A and B types are too low. Lanthanum and cerium give only type A, as the transition to B takes place at too low a temperature. The stability of the three types is shown in Fig. 53 (after Goldschmidt).

It thus appears that there is no fundamental distinction between the cerium and yttrium earths, but that the observed differences depend on temperature; this applies to the salts as well as to the oxides. In the classical separation of the rare earths this was not noticed owing to the working temperatures being between 20° and 100°.
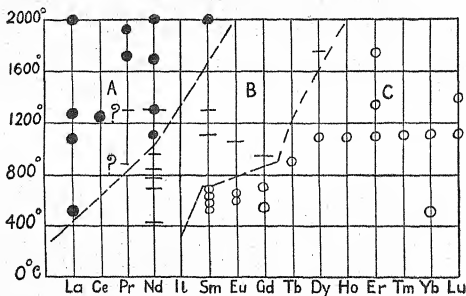
FIG. 53.—Ranges of stability of the rare earth oxides.

The oxides of the cerium group are the most electropositive, and a decrease of basicity is observed in the series La, Pr, Nd, Ce^{III}; Y; the terbium earths; the ytterbium earths; Sc, Ce^{IV}. The basicity decreases with increasing atomic number, but the elements with atomic numbers falling far beyond those of the remainder of the series (Y, Sc), do not occupy a terminal position, again owing to the lanthanide contraction. Hopkins[1] gives the following relative strengths of the hydroxides, taking $Y(OH)_3$ as unity:

Element		Y	La	Pr	Nd	Sm	Gd	Dy
At. Number		39	57	59	60	62	64	66
Basicity		1	1300	80	47	8	3·4	0·5

$La(OH)_3$, the strongest known tervalent base, is sixteen times as basic as $Pr(OH)_3$, and thereafter the fall in basic strength is rapid. The low basicity of quadrivalent cerium follows naturally from its valency.

Separation of the Rare Earths by Difference of Basicity.—This gradation in basicity may be used to separate the rare earths from each other. If a solution of mixed salts is precipitated by small quantities of solutions containing hydroxyl ions, the weakest bases separate first

[1] *J. Chem. Educ.*, 1936, **13**, 363.

(ytterbium earths), then the stronger ones (terbium earths), and, last of all, the strongest ones (cerium earths). If this fractional precipitation is repeated and the individual fractions again fractionated, the last fractions of the first precipitation being combined with the first of the second, and this combination then fractionated, then after much repetition not only can the individual groups be finally separated from each other, but their individual members can also be isolated. This process has been successfully carried out, particularly in the ytterbium earth group, without, however, coming with certainty to an end-fraction which is truly homogeneous (cf. p. 436). Caustic soda, ammonia and magnesia have been employed as precipitating bases, but the oxides of the rare earths can themselves be used with especial advantage. A small quantity of the mixture to be separated is converted to the oxide, and then added to the main portion, which is present as a salt in solution. The least basic constituents are precipitated by the oxide which has been added, while the most basic constituents of the added oxide go into solution again. The earths are precipitated as basic salts and not as oxides. This process is comparable to the separation of electronegative metals from their solutions by the introduction of more electropositive ones; the oxides can be arranged in a similar electro-chemical series which governs the separation and solution of the individual members.

The difference in the basicity may be turned to account in yet another way. It is well known that the nitrates of weak bases decompose into the basic oxides more easily when heated than those of strong bases. If a mixture of rare earth nitrates is heated, first at a low temperature and then at a higher, the ytterbium group nitrates decompose first, the terbium nitrates later, and the cerium nitrates last; the difference between the decomposition temperatures within the individual groups is also considerable. The nitrates which are still undecomposed may be separated by extraction with water, a process which is further facilitated by the fact that the basic nitrates of the cerium earths are soluble in water, whereas the basic ytterbium nitrates are insoluble. Such basic nitrates are formed as primary decomposition products before the oxides are produced. For separation by crystallisation cf. p. 433.

All the rare earth metals can be precipitated as their 8-hydroxy-quinoline compounds and regulation of pH permits the separation of cerium, thorium and yttrium from the mixture.[1]

Separation of the Rare Earths from Other Elements. Oxalate Method.—Before the isolation of the rare earths is commenced they must first be separated from the common elements with which they are associated. This separation is usually carried out by the oxalate or sulphate methods. The oxalates of the rare earths differ from all other oxalates in being very difficultly soluble in mineral acids; the

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[1] Manelli, *Atti X. Congr. intern. Chim*, 1938, II. 718.

separation, therefore, is easily performed by adding ammonium oxalate
to an acid solution of the earth minerals. The oxalates which separate
are sticky and lumpy at first, but soon become crystalline.

Only zirconium and thorium are precipitated with the rare earths in this opera-
tion ; but their oxalates, unlike those of the other earths, dissolve easily in excess of
ammonium oxalate, so that they can be separated in this way. The difficult solubility
of the earth oxalates probably depends on complex formation. The oxalates which
separate are not simple, but the salts of oxalo-acids or the oxalates of oxalato-bases,
as they easily give mixed salts, *e.g.* chloro-oxalates, when decomposed with other
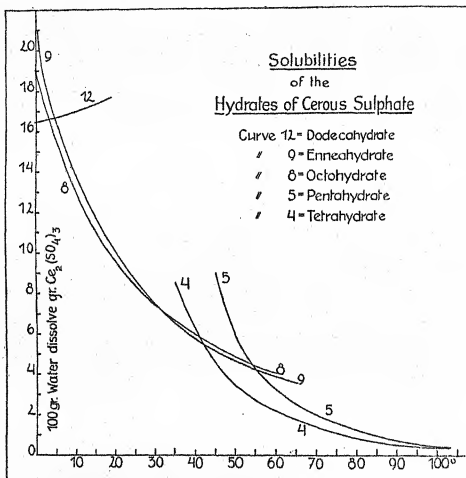
Fig. 54.

acids. This tendency to form auto-complex compounds is often met with in the
rare earths (*cf.* pp. 290 and 344).

The oxalates are not altogether insoluble in acids. Their varying solubility in
dilute acids has been employed in the separation of the earths, particularly of those
of the cerium group, but without very favourable results.

Sulphate Method.—The separation of the rare earths as sulphates
is based on the observation that these sulphates are much more soluble
in cold than in hot water. Calcium salts, particularly the sulphate, and
many other sulphates (*e.g.* anhydrous sodium sulphate) show a decrease
in solubility with rising temperature; but this is nowhere so marked
as in the sulphates of the rare earths. The separation is further
favoured by the formation of very highly supersaturated solutions by

the lower hydrates of the sulphates, which have the greatest solubility. If, *e.g.*, cerous sulphate is dehydrated, which can be carried out at temperatures up to 500° without loss of SO_3, and the anhydrous residue is dissolved in ice water, 100 parts of water take up 60 parts of salt. This solution, when warmed, is supersaturated with reference to the dodecahydrate, and still more with reference to the other hydrates. The diagram on p. 432 (Fig. 54), after Koppel,[1] shows clearly the behaviour of cerous sulphate in solution. On account of the easy supersaturation the various portions of the curve may be followed far beyond the transition points.

In general the solubility of the hydrates (the anhydrous salt is not included) decreases with rising temperature—only the dodecahydrate dissolves better at higher temperatures. Similar types to the 4-, 8- and 12- hydrates are also found in the sulphates of the other rare earths. Thorium sulphate also shows decreasing solubility with rise of temperature.

Separation by Crystallisation.—Double sulphates are better for effecting separations than are the simple sulphates; they are of the type $M^I_2SO_4$, $M^{III}_2(SO_4)_3$, 8 (or less) H_2O, and are formed by all the earths. Double sulphates similar to the alums are not known, some of those of the cerium earths, especially those of cerium itself (*cf.* p. 583), are difficultly soluble in solutions of alkali sulphates, while those of the ytterbium earths are easily soluble. In this way a very good separation of the two classes may be attained, though not with a sharp line of demarcation, but only with a gradual transition. If a crust of sodium sulphate is introduced into the sulphate solutions the double sulphates separate in the order of their insolubility. Acid sulphates can also be formed.

The fractional crystallisation is more favourably carried out with the double nitrates than with double sulphates. This method permits of the separation of the individual earths from each other, rather than from foreign metals, and in the hands of Auer von Welsbach[2] has made the present knowledge of the rare earths possible. He separated didymium, which was previously considered an element, into praseodymium and neodymium, and later and almost simultaneously with Urbain, split ytterbium into lutecium and (neo)ytterbium. This method has been proved to be best for separating the cerium earths.

All the cerium earths form double nitrates with uni- and bi-valent metals, to which the general formula $2M^INO_3$, $M^{III}(NO_3)_3$ is given. Their separation is not different in principle from ordinary fractional crystallisation, but the method is noteworthy, since in order to attain the goal thousands of crystallisations are necessary, of which the

[1] *Z. anorg. Chem.*, 1904, 41, 377.
[2] *Monatsh.*, 1884, 5, 1 ; *Ber. Wien. Akad.* (II.), 1884, 88, 1237.

merely manual control demands rigid systematisation. This is carried out in the following way:

The initial material which must weigh several kilograms in order to obtain a sufficient quantity of a pure end-product, is first crystallised and six or eight successive crops isolated, leaving the mother liquor. Each crop is again crystallised, when the less soluble portion crystallises out, and the more soluble remains in the mother liquor. The mother liquor of crop 1 is mixed with the crystals which have separated from crop 2, the mother liquor of crop 2 is mixed with the crystals which have separated from crop 3, etc. Each of these mixtures is again split up into crystals and mother liquor, which are then again mixed with the

FIG. 55.—Fractional crystallisation of the rare earths.

neighbouring series in such a way that the mother liquor of the more sparingly soluble crop is mixed with the crystals of the next more soluble kind. The number of fractions therefore increases in each series, for the initial crops meet no mother liquors with which to combine, and are therefore themselves split up into a new crop and a new mother liquor. When this process has been repeated a number of times and a large number of fractions obtained, the terminal members of the extensive work are always removed: the first crops of the first fractions are separated, and contain the most sparingly soluble portions. Likewise, the last mother liquors are not decomposed further; they contain the most soluble components. The number of fractions thus gradually diminishes, and only those of medium solubility remain to be worked up. If the earths from lanthanum to terbium are worked up the procedure shown in Fig. 55 (above) is used, in which ● denotes crystal crops, and ○ the mother liquors.

The most soluble constituents are separated here as mother liquors,

the most sparingly soluble as crystals, and those of medium solubility form fractions which contain crystals as well as mother liquors.

When Auer von Welsbach fractionated a supply of "didymium" in this way, he found that the initially colourless mass gradually became coloured: green praseodymium became concentrated in the sparingly soluble fractions, and rose-coloured neodymium in the easily soluble ones. The colours of the salts are complementary, so that a mixture of them appears colourless in "didymium," just as in a suitable mixture of a green nickel and a pink cobalt salt neither of these colours may be recognised. In order to separate praseodymium and neodymium it is generally advisable not to undertake the cerium separation, or at least not to carry it to completion, although that

FIG. 56.—Percentages of rare earths in minerals.

can easily be done beforehand. Cerium appears during the crystallisation of the middle fractions between praseodymium and neodymium, and so facilitates their complete separation. It can be removed afterwards just as easily as before the separation of the other two elements.

It is very remarkable that a single method never, or very seldom, gives a complete separation of the rare earths. It is common to obtain fractions which cannot be further decomposed. If a second method is then employed the decomposition proceeds further. For this reason several methods of crystallisation must be used in succession, or alternation between crystallisation and precipitation methods (p. 430) Many errors in the chemistry of the rare earths might have been avoided if it had been noticed earlier that the terminal members, formed after the application of one method, may be split up further by using another method.

In order to effect an adequate separation hundreds of kilograms of the initial material is required. Europium, for example, which is

merely manual control demands rigid systematisation. This is carried out in the following way:

The initial material which must weigh several kilograms in order to obtain a sufficient quantity of a pure end-product, is first crystallised and six or eight successive crops isolated, leaving the mother liquor. Each crop is again crystallised, when the less soluble portion crystallises out, and the more soluble remains in the mother liquor. The mother liquor of crop 1 is mixed with the crystals which have separated from crop 2, the mother liquor of crop 2 is mixed with the crystals which have separated from crop 3, etc. Each of these mixtures is again split up into crystals and mother liquor, which are then again mixed with the

FIG. 55.—Fractional crystallisation of the rare earths.

neighbouring series in such a way that the mother liquor of the more sparingly soluble crop is mixed with the crystals of the next more soluble kind. The number of fractions therefore increases in each series, for the initial crops meet no mother liquors with which to combine, and are therefore themselves split up into a new crop and a new mother liquor. When this process has been repeated a number of times and a large number of fractions obtained, the terminal members of the extensive work are always removed: the first crops of the first fractions are separated, and contain the most sparingly soluble portions. Likewise, the last mother liquors are not decomposed further; they contain the most soluble components. The number of fractions thus gradually diminishes, and only those of medium solubility remain to be worked up. If the earths from lanthanum to terbium are worked up the procedure shown in Fig. 55 (above) is used, in which ● denotes crystal crops, and ○ the mother liquors.

The most soluble constituents are separated here as mother liquors,

the most sparingly soluble as crystals, and those of medium solubility form fractions which contain crystals as well as mother liquors.

When Auer von Welsbach fractionated a supply of "didymium" in this way, he found that the initially colourless mass gradually became coloured: green praseodymium became concentrated in the sparingly soluble fractions, and rose-coloured neodymium in the easily soluble ones. The colours of the salts are complementary, so that a mixture of them appears colourless in "didymium," just as in a suitable mixture of a green nickel and a pink cobalt salt neither of these colours may be recognised. In order to separate praseodymium and neodymium it is generally advisable not to undertake the cerium separation, or at least not to carry it to completion, although that

FIG. 56.—Percentages of rare earths in minerals.

can easily be done beforehand. Cerium appears during the crystallisation of the middle fractions between praseodymium and neodymium, and so facilitates their complete separation. It can be removed afterwards just as easily as before the separation of the other two elements.

It is very remarkable that a single method never, or very seldom, gives a complete separation of the rare earths. It is common to obtain fractions which cannot be further decomposed. If a second method is then employed the decomposition proceeds further. For this reason several methods of crystallisation must be used in succession, or alternation between crystallisation and precipitation methods (p. 430) Many errors in the chemistry of the rare earths might have been avoided if it had been noticed earlier that the terminal members, formed after the application of one method, may be split up further by using another method.

In order to effect an adequate separation hundreds of kilograms of the initial material is required. Europium, for example, which is

not one of the rarest earths occurs only to the extent of 0·0002 per cent. in monazite sand. The determination of the atomic numbers of the metals of the rare earths by Moseley[1] and of the mass spectra by Aston (cf. p. 30) indicates clearly their chemical individuality. Illinium was claimed to be detected spectroscopically by Harris, Hopkins and Yntema,[2] and also by Rolla and Fernandes,[3] who called it florentium. A careful survey by other workers notably Prandtl[4] and I. Noddack[5] has served to render negative the evidence of the earlier workers. It is considered possible that No. 61 is radioactive and unstable, for samarium (No. 62) is radioactive[6]; also it may be almost exclusively bivalent, for bivalent compounds of its cogeners, samarium and europium are known. An examination of minerals containing the alkaline earths, however, has failed to reveal its presence.

The relative plentifulness of the rare earths is in remarkable agreement with the rule of W. D. Harkins[7] that elements of odd atomic number are always less plentiful than those of even atomic numbers which immediately precede or follow them. This rule applies equally well to other elements, but is more obvious in the later series of the periodic system. In Fig. 56 (p. 435) the quantities of the various earths present in a large number of minerals have been averaged by Goldschmidt, the quantity of earths present being represented by percentage × 10⁶. Although some members of this group are scarce, nevertheless the group as a whole is as plentiful in nature as lead, and cerium, the most abundant element of the group, is commoner than silver.

Tests of Purity.—There are several methods for finding out whether a product requires still further fractionation; the equivalent weight of the fractions obtained may be estimated, the spectrum examined or the magnetic susceptibility measured.[8] The first method is applied in this way : the oxalates or sulphates which are prepared from the fractions are converted to the oxides at red heat, and it is observed whether the ratio weight of oxalate/weight of oxide, or weight of sulphate/weight of oxide changes on further fractionation. The atomic weights of some of the earths, especially those in the ytterbium group, are so little different from each other that a change in the relative quantities would not be noticeable in the fractions. For practical reasons the conversion of the oxide into the sulphate is preferred to that of the sulphate into the oxide, as the whole of the SO_3 is not driven off from the sulphates below 1000°. If this temperature is not reached stable compounds of the formula $M_2O_3 . SO_3$ are obtained over a range of

[1] *Phil. Mag.*, 1914, **27**, 710.   [2] *J. Amer. Chem. Soc.*, 1926, **48**, 1594.
[3] *Gazzetta*, 1926, **56**, 435.   [4] *Z. angew. Chem.*, 1926, **39**, 897, 1333.
[5] *Ibid.*, 1934, **47**, 301.   [6] von Hevesy and Pahl, *Nature*, 1932, **130**, 846.
                    [7] *J. Amer. Chem. Soc.*, 1917, **39**, 856.
                    [8] See Pearce, *Chem. Reviews*, 1935, 121.

several hundred degrees, corresponding to $Ce_2O_3 . CO_2$, which is obtained by incomplete ignition of the carbonate.

The **spectroscopical examination** is carried out by observing the absorption or emission spectra. The absorption spectra given by solutions of the coloured rare earths are specially characteristic, and differ from those of all other elements by the rather sharp demarcation of the bands from the non-absorbed portion of the spectrum. The absorption spectra of the earths almost give the impression of reversed line spectra, with lines broader than those in emission spectra. They are, however, few in number, and their position is very characteristic, so that an expert can recognise the elements from the position of the lines without accurately measuring them. The tendency of a simple rare earth salt to become complex, especially in concentrated solution, reduces the sharpness of the method. The complex compounds have different spectra from the simple ions, so that the position of the spectrum changes with concentration, and also with temperature, since rise in temperature diminishes the formation of complexes. The solvent also has an effect; *e.g.* alcohol favours auto-complex formation more than water.

The formation of distinct reflection spectra is also characteristic of solid bases which contain the earths. If a spectroscope is directed on to an illuminated mineral containing the earths, the absorption spectra are seen just as if the light were passing through a solution of their salts. Again, the spectra of different compounds of the same earth are not quite the same, but become more violet when the metal atom is claimed by the anion. This effect depends on the polarising action of the anion (*cf.* p. 231) which causes a contraction. The colours of the rare earths are certainly dependent on the condition of the inner incomplete level of electrons; and if the energy relations are such that this colonisation by electrons demands a greater expenditure of energy, the spectrum shifts towards the short wave-length end. The following table [1] shows the position of the three most important lines in the praseodymium spectrum as found in its four halides:

	I.	II.	III.
PrI_3	456·5	482·1	495·9 mμ
$PrBr_3$	453·2	478·0	493·0
$PrCl_3$	450·3	475·5	489·8
PrF_3	442·5	468·0	480·3

The emission spectra are much richer in lines than the absorption spectra, and an exact examination is as troublesome as for other elements. Flame, spark or arc spectra are used. The flame spectrum of the colourless earths is continuous, while the position of the discontinuous bands of the coloured earths is exactly similar to that of

[1] F. Ephraim and R. Bloch, *Ber.*, 1926, 59, 2692; 1927, 61, 65.

the absorption spectra of their solutions. This astonishing effect is
without parallel in spectroscopical observations. The colourless earths
also give lines in the spark spectrum, which are more characteristic of
them than those of the coloured earths. The arc spectra are the most
characteristic, and here too those of the white earths are more conspicuous
than those of the coloured ones.

The phosphorescence or cathode luminescence spectra were also
previously used for characterisation, but they are very strongly
influenced by traces of impurities. The perfectly pure earths generally
give no discontinuous cathode luminescence spectra, and the large
number of elements (meta-elements) deduced by Crookes from the
heterogeneity of the phosphorescence spectra was due to the influence
of foreign substances.

Separation of Cerium.—The separation and preparation of pure
cerium is specially facilitated by the ease with which this element, in
contrast to the others, can be converted to the quadrivalent form.
Ceric hydroxide, the weakest base of all (p. 430), may be precipitated
by weak alkalis, and so separated from the others. The solution of
the tervalent earths is treated with potassium permanganate to
oxidise the cerous salt to $Ce(OH)_4$, which is precipitated together
with manganese, when the solution is made very slightly alkaline.
Alternatively, chlorine may be passed into an aqueous suspension of the
hydroxides; the cerous hydroxide is then oxidised to ceric, while the
others form chlorides and hypochlorites, and remain as such in solution.
Yellow ceric sulphate, $Ce(SO_4)_2$, is preferably used for isolation by
hydrolysis, but a portion remains in solution, so that loss is incurred.
The product, however, is very pure, while the oxidation method, although
it certainly permits of the easy separation of the whole of the cerium,
gives it only in an impure form, mixed with other earths. It may then
be purified, *e.g.* by means of the orange-red ceric ammonium nitrate,
which is fairly insoluble in concentrated nitric acid. In spite of the
relatively simple separation, several methods must be employed
successively in order to obtain a substance which gives a very pale
coloured cerium dioxide, which is the criterion for the absence of other
earths (p. 428).

A useful method is the anodic oxidation of cerium oxalate or nitrate
solutions. On addition of a soluble phosphate to the oxidised solution,
ceric phosphate is precipitated and subsequently purified.

Separations based on Conversion to the Bivalent Condition.—Just as
the variable valency of cerium makes possible its ready separation from
the others, so also the reduction of europium, ytterbium and samarium
to the bivalent condition is valuable; in this condition, their sulphates
resemble those of barium and strontium. Yntema[1] separated almost
pure, colourless, $EuSO_4$ from gadolinium by electrolytic reduction of

[1] *J. Amer. Chem. Soc.*, 1930, 52, 2782.

the chloride solution in presence of sulphuric acid. Bell and Yntema[1] have shown that pale green $YbSO_4 . xH_2O$ can be similarly separated from mixtures with yttrium, erbium and thulium. McCoy[2] reduced $EuCl_3$ to $EuCl_2$ by the action of zinc and acid, and Jantsch, Skalla and Grubatsch[3] showed that the trichlorides of Eu, Yb and Sm are reduced to dichlorides by hydrogen at $270°$, $560°$ and $1000°$ respectively.

Hafnium

If the table showing the grouping of the electrons in the atoms of the elements (p. 6) and also the classification of Bohr (p. 25) are studied, it will be seen that the properties of element No. 72 are likely to be different from those of the rare earths which immediately precede it In the sequence from lanthanum (57) to lutecium (71) it is the fourth shell of electrons which is augmented, while the shells outside that layer remain unaltered in structure. In consequence the valency, which is largely determined by the outermost electrons, remains generally constant until, in lutecium, the fourth shell is completed. Additional electrons in elements with numbers higher than 71 must lie in shells more remote from the nucleus, and thus function as valency electrons. Element 72 is not, therefore, one of the rare earths, as was previously supposed, but a quadrivalent element occupying a place below zirconium in the fourth group.

Acting on these considerations, which were advanced by Bohr. Coster and v. Hevesy[4] examined the X-ray spectra (p. 8) of a number of zirconium minerals and found that almost all of them contained from 1 to 24 per cent. (usually about 5 per cent.) of a new element, which they named hafnium (Hafniae: Copenhagen).

The separation of hafnium from zirconium is carried out by the fractional crystallisation of the double alkali fluorides, $M_2Hf(Zr)F_6$ and $M_3Hf(Zr)F_7$, or oxalates, when the hafnium remains in the mother liquor. The chemical properties of hafnium and zirconium are very similar, and there is a much closer relation between these two elements than between hafnium and thorium, the element which comes after it in the fourth group (*cf.* lanthanide contraction, p. 424). Hafnium and zirconium are thus found to accompany each other in minerals, though the new element is not found in thorium or titanium minerals which do not contain zirconium. A property common to both hafnium and zirconium is the insolubility of their phosphates in concentrated acids, in which they differ from all other elements. Hafnium phosphate $HfO(H_2PO_4)_2$ is appreciably less soluble than that of zirconium, and if fractionally precipitated eight times, the zirconium is freed from

[1] *J. Amer. Chem. Soc.*, 1930, 52, 4264.
[2] *Ibid.*, 1936, 58, 1577.   [3] *Z. anorg. Chem.*, 1933, 216, 75.
[4] *Ber.*, 1923, 56, 1503 ; *Nature*, 1923, 111, 79.

hafnium. Solutions of hafnium salts are also more readily precipitated by ammonia, thiosulphates or salicylates than those of zirconium. Zirconium may be freed from hafnium by utilising the properties of the double chlorides $2ZrCl_4 . PCl_5$ and $2ZrCl_4 . POCl_3$ which distil undecomposed and have higher boiling points than the corresponding hafnium compounds. In these properties hafnium is not intermediate between zirconium and thorium.

In its general chemical properties hafnium, as the heavier metal, is more basic than zirconium. Thus hafnium sulphate begins to decompose at $500°$, while zirconium sulphate is broken down at $400°$. The chloride, again, volatilises with that of zirconium at about $250°$, but the first fractions are richer in $ZrCl_4$. The density of hafnium dioxide is 9·67, in contrast to that of zirconium (5·73), if both are prepared by ignition of the normal sulphate at $1000°$. The physical similarity between zirconium and hafnium is shown, however, in the closeness of the b.pts. of the oxides: ZrO_2, $2950°$; HfO_2, $3050°$ T.

BASIC OXIDES OF THE HEAVY METALS

*Oxides of the metals from Al to Cu in the electrometric series—Preparation and
stability—Properties—Hydroxides—Compounds with bases—Oxides of the noble
metals—Their ammines*

Oxides of the Metals from Aluminium to Copper in the Electrometric Series

THE electrometric series (p. 151) is not a good guide to the affinity
of the elements for oxygen. The condensation to solid oxide, and the
breaking-up to form ions in solution are processes which give rise to
very different energy changes. The table which follows gives the heat
of formation (in Cals.) of the commonest oxide, from a gram atom of
oxygen and the equivalent quantity of the metal. The heat of forma-
tion of the sulphides is given for comparison, and it may be noted that
the order for the sulphides is not that of the oxides nor that of the
electromotive series.

	Oxide.	Sulphide.		Oxide.	Sulphide.		Oxide.	Sulphide.
Y	158	...	B	90·9	12·6	H	58·1	...
La	148·2	...	Mn	90·0	45·6	Sb	55·6	11·5
Mg	145·5	79·4	Zn	84·8	43·0	As	52·1	...
Li	145	...	P	73·1	...	Pb	50·8	20·3
Ca	145	104·3	Sn	70·6	...	Bi	46·4	...
Sr	131·2	99·3	C	68·2	...	Cu	43·8	21·7
Al	128·6	42·0	Cd	66·3	34·4	Th	42·8	20·3
Na	100·9	89·3	Fe	65·9	24·0	S	34·6	...
K	98·2	103·5	W	65·7	...	Hg	21·5	10·6
Rb	95·5	...	Co	64·5	21·9	Ag	7·0	3·0
Si	90·9	5·2	Ni	61·5	19·5			

It may be seen, however, that the middle elements of that series are
also in the middle of the oxide series, though the order is different;
the hydroxides follow the electrometric series rather more closely than
the oxides themselves.

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The following are the more important of the oxides of the metals to be considered here:

	Ga_2O		Tl_2O			Cu_2O			
		InO		ZnO	CdO	CuO	PbO	TiO	MnO
Al_2O_3	Ga_2O_3	In_2O_3	Tl_2O_3				Pb_2O_3		Mn_2O_3
							Pb_3O_4		Mn_3O_4
							PbO_2		MnO_2

FeO	NiO	CoO	GeO	SnO	VO				CrO
Fe_2O_3	Ni_2O_3	Co_2O_3			V_2O_3	Mo_2O_3			Cr_2O_3
Fe_3O_4	Ni_3O_4	Co_3O_4							
					VO_2	MoO_2	WO_2	UO_2	

The oxides of the rare earth metals are discussed on p. 423 *et seq.*, the dioxides of Zr, Th, Ge and Sn on p. 812 *et seq.*, and the higher metallic oxides with acidic properties in Chaps. XVI and XVII.

Preparation and Stability.—The oxides of the metals of this group can be prepared in the following ways:

1. Oxidation of the metal or of a lower oxide.

2. Reduction of higher oxides with hydrogen, carbon monoxide, etc.

3. Decomposition of the corresponding hydroxides, carbonates, nitrates or oxalates by heat:

$$M(OH)_2 \longrightarrow MO + H_2O \qquad\qquad MCO_3 \longrightarrow MO + CO_2$$
$$M(NO_3)_2 \longrightarrow MO + 2NO_2 + O \qquad MC_2O_4 \longrightarrow MO + CO_2 + CO.$$
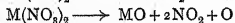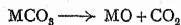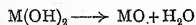
The formation of oxides by oxidation of the metal takes place most readily when the metal is volatile, like zinc, cadmium, indium and thallium. The vapour is so rapidly oxidised on passing into the air that a flame is produced—zinc burns with a greenish-blue flame, cadmium gives a dark red, indium a deep blue, and thallium a bright green flame. The highest oxide is formed in this way in a very fine state of division. Zinc, in particular, gives a very finely powdered oxide under these conditions (hence the names lana philosophica and flores zinci); it is not necessary to isolate the metal in order to obtain the oxide; if a zinc ore is heated with anthracite in a current of air the volatile zinc is rapidly oxidised.

The other metals of this group burn only when finely divided—cobalt with a red light, and iron with bright flashes, especially when introduced into pure oxygen. The combustion of the iron is, however, mainly superficial when the metal is in the liquid or solid state so that a flame, which implies the existence of the element in the gaseous state, is then absent. The change of copper to cupric oxide, which takes place quietly in the air below red heat, is typical of the usual phenomena. It might be expected that the oxides would be formed at the ordinary temperature, for they are all strongly exothermic, but the layers of oxide protect the metal from

further attack. The retardation of the oxidation often depends on the state of the surface of the metal, as shown by nickel, aluminium or chromium; when they are left in the air, after receiving a fine polish, oxidation is thereby prevented and they remain untarnished for a long time. The renewal of the surface is most readily carried out when the metals are fused. In the preparation of lead oxide (massicot) a current of air is passed over the surface of the fused metal and the skin of oxide removed from the surface as fast as it forms. Chromous oxide, CrO, is prepared by the oxidation of chromium amalgam in the air. When the surface of a metal is rough, oxidation takes place even in the solid form, and the greater the specific surface the faster the oxidation proceeds. Very finely divided metals oxidise so rapidly in the air that they catch fire spontaneously; the metals are obtained in this pyrophoric form by the reduction of oxides with hydrogen, the oxides being obtained by decomposing the oxalates at a low temperature. Lower oxides are also sometimes pyrophoric—for example, FeO, V_2O_3, InO made by hydrogen reduction, or the CrO obtained by oxidation of the amalgam. They are converted into the higher oxides on heating them in the air, or even when simply left exposed to air.

When a metal forms several oxides the oxygen dissociation pressure determines which will be formed at a given temperature. The partial pressure of oxygen in the air is 0·2 atm., and if the oxides of lead are taken as an example it is found that only the lower oxide, PbO, is stable in air above 550°, while Pb_2O_3 is stable from 450° to 550°, and Pb_3O_4 exists between 350° and 450°, and is formed when either PbO or PbO_2 is brought to this temperature. Unconverted PbO can be extracted with acetic acid or alkali acetate solution. PbO_2 is stable at lower temperatures, and although the formation of red lead, Pb_3O_4, is a reaction which can be reversed in practice, the dioxide cannot be formed from the monoxide at low temperatures. The reactions of the solid oxides with gases are often very slow, and carbon dioxide is taken up only to a very slight extent by PbO, and even less by other oxides. The oxides can therefore be prepared by the dehydration of the hydroxide or by heating the carbonate, even when the oxide produced is normally changed in air to a higher oxide. For instance, when manganese hydroxide, $Mn(OH)_2$, is heated, MnO is formed, although this oxide is only stable at the atmospheric oxygen pressure at a white heat, and can only be obtained from Mn_3O_4 if this temperature is reached. Mn_3O_4 is the oxide obtained on heating the other oxides in air with the Bunsen burner, and is therefore used in the analytical determination of manganese. If the oxygen pressure is artificially raised, as when the heating is carried out in pure oxygen, Mn_2O_3 and even MnO_2 can be obtained at temperatures when Mn_3O_4 is the oxide stable in air. The dioxide can be prepared from compounds which

decompose at low temperatures, e.g. $Mn(NO_3)_2$, which leaves MnO_2 when heated to 190°. This oxide can also be obtained from the lower oxides when they are prepared in the pyrophoric form and then aerated—MnO prepared by gentle heating of the oxalate oxidises rapidly in the air to the dioxide.

The oxides of cobalt are related in a similar way to one another. Co_2O_3 is obtained when the nitrate is gently heated, but it is converted to Co_3O_4 on strongly heating with the Bunsen burner, as is also the lowest oxide CoO. The monoxide, on the other hand, is formed from Co_3O_4 when it is heated in the air to 905°. The range of existence of Co_3O_4 is more restricted than that of the corresponding oxide of manganese, and it is therefore less reliable for analytical purposes unless the temperature to which it is heated is carefully regulated.

The higher oxides of nickel are more readily decomposed than those of cobalt: Ni_2O_3, obtained from the nitrate, gives off oxygen readily, giving Ni_3O_4. This oxide, however, is stable only up to 240°, and can be prepared by fusing nickel itself with sodium peroxide. The monoxide obtained by igniting Ni_3O_4 retains additional oxygen with some tenacity, and must be ignited strongly for some time if it is to be weighed in analytical work. The conversion of NiO to Ni_3O_4 by heating in air is not feasible, although the analogous oxidation of MnO and CoO can readily be carried out. The decomposition temperature of Fe_2O_3, again, is so high that it cannot be attained by any of the ordinary methods of heating, and both FeO and Fe_3O_4 are converted into this oxide over a very wide temperature range. Even when finely divided FeO, obtained by hydrogen reduction of Fe_2O_3, is exposed to the air it is oxidised to Fe_2O_3 and not to Fe_3O_4. Vanadium pentoxide is converted into the trioxide at 1750°, Tl_2O_3 passes into Tl_2O at 699°, and CrO_3 is reduced to Cr_2O_3 just above 200°.

The oxygen dissociation pressure of the copper oxides has been determined at various temperatures. CuO has a pressure of 118 mm. at 1000°, and 458 mm. at 1070°. The decomposition leaves a solid solution of Cu_2O in CuO, and in consequence the pressure decreases gradually. Similar solid solutions are met with in the oxides of iron; it is, for instance, only a matter of chance that "hammer scale" has the composition Fe_3O_4.

The final decomposition of the oxides of these metals into their elements takes place only at very high temperatures; as a class they are intermediate between the easily decomposed oxides of the noble metals and the still more stable oxides of the alkali and alkaline earth metals. Cu_2O is the most easily decomposed—at 1935° T. at the ordinary pressure of oxygen in the air. The dissociation pressure of ZnO only reaches the value of 0·2 atm. at the very high temperature of 3817° T.

The dissociation pressures of some of these oxides were determined

by Wöhler and Balz,[1] by utilising the equilibrium between the metal and steam : $M + H_2O \rightleftharpoons MO + H_2$. The pressure is very small in all the oxides examined :

	Temperature (° C.)	O$_2$ Pressure in mm.
1. (a) Fe$_2$O$_3$ . . .	427	$2 \cdot 241 \times 10^{-26}$
(b) Fe$_3$O$_4$ . . .	725	$4 \cdot 25 \times 10^{-17}$
	950	$1 \cdot 49 \times 10^{-11}$
(c) FeO	750	$1 \cdot 602 \times 10^{-17}$
	990	$1 \cdot 984 \times 10^{-12}$
2. (a) Co$_3$O$_4$ . . .	450	$3 \cdot 160 \times 10^{-56}$
(b) CoO . . .	450	$4 \cdot 574 \times 10^{-26}$
3. NiO . . .	450	$5 \cdot 181 \times 10^{-26}$
4. (a) CuO . . .	450	$1 \cdot 963 \times 10^{-26}$
(b) Cu$_2$O . . .	450	$7 \cdot 561 \times 10^{-26}$
5. Mn$_3$O$_4$ . . .	450	$2 \cdot 941 \times 10^{-26}$
6. (a) SnO$_2$ . . .	800	$2 \cdot 107 \times 10^{-13}$
(b) SnO . . .	800	$6 \cdot 771 \times 10^{-14}$
7. (a) WO$_3$ . . .	800	$1 \cdot 54 \times 10^{-13}$
(b) W$_2$O$_5$ . . .	800	$1 \cdot 555 \times 10^{-14}$
(c) WO$_2$ . . .	800	$1 \cdot 693 \times 10^{-16}$
	1000	$4 \cdot 91 \times 10^{-12}$

The pressures obtained with CuO and Cu$_2$O, SnO and SnO$_2$ are interesting. On account of the slight differences, CuO is formed in the oxidation of copper as well as Cu$_2$O, and with tin, SnO$_2$ is the main product.

The reduction of the oxides to lower oxides or to the metal can take place at quite low temperatures in the presence of a substance which has a strong affinity for oxygen. Carbon usually brings about reduction to the metal, but in a few cases the lower oxide only is formed. For example, alkali chromates are reduced to Cr$_2$O$_3$ when heated with starch. After carbon, the most useful reducing agents are hydrogen (free, or obtained by the dissociation of ammonia at the temperature of reduction) and carbon monoxide, or a mixture of the two as water-gas. The equilibrium between carbon monoxide and the various oxides of the metals is of great importance in the working of blast furnaces (p. 196), and various reduction products can be obtained by working at different temperatures. When they exist, lower oxides are always formed by operating at low temperatures. This is often the most practicable way of making the lower oxides, especially when complete reduction to the metal is difficult (e.g. VO, V$_2$O$_3$, NiO, MoO$_2$, WO$_2$, UO$_2$). Lower oxides may also be obtained by heating a higher oxide with the metal in a current of hydrogen, e.g. Ga$_2$O from a mixture of Ga$_2$O$_3$ and Ga ; the lower oxide is a strong reducing agent. Reduction to the metal, when hydrogen is used, takes place below 200° for Co, at just above 100° for lead, for cadmium at 290°, for Cu at 150°, and for Zn at 450°. When carbon monoxide is used

as the reducing agent the reduction temperatures are even lower. It would be misleading to give accurate minimum temperatures at which the oxides are reduced to metal, for the reaction takes place in many cases at the ordinary temperature, but at such a slow rate as to be imperceptible.

As is well known, the reaction $M + H_2O \rightleftharpoons MO + H_2$ is a reversible process in this group, so that while hydrogen provides a means of obtaining the metal from the oxide, steam can be used as an oxidising agent for the formation of the oxide. The reaction from right to left takes place more readily at lower temperatures, the reverse process at higher temperatures. Iron is again a typical example of an element which undergoes this kind of reaction; the magnetic oxide Fe_3O_4, which is not easily made in other ways, is obtained when steam is passed over red hot iron. Cobalt gives CoO under similar treatment.

The decomposition of ammonium dichromate is an interesting example of the reduction of a higher oxide to a lower by the use of ammonia. If one point in a heap of this salt is touched with a hot needle a glow starts from that point and pervades the whole mass, which swells very markedly. The CrO_3 is reduced (approximately) to Cr_2O_3 by the ammonia in the compound.

The formation of oxides by dehydrating the hydroxide is the more readily carried out the more electronegative (noble) the metal it contains. The decomposition can hardly be caused to take place at all in the hydroxides of the alkali metals, while in the alkaline earths fairly high temperatures are necessary to remove the water. The hydroxides of the noble metals, on the other hand, lose water with formation of the oxides even at room temperature. The group of metals discussed in this section shows an intermediate behaviour between these two extremes. The hydroxides of aluminium and zinc lose their water almost completely at a few hundred degrees, while those of some of the other metals are decomposed at 100°. The most important of these are the hydroxides of copper, which in the univalent state behaves like the noble metals and gives no stable hydroxide. Cuprous oxide is obtained direct by the precipitation of a solution of a cuprous salt with alkali, or on the reduction of an alkaline cupric solution (Fehling's solution) by such reducing agents as hydroxylamine or dextrose. The precipitate formed in the cold is yellow and on warming is converted into red crystalline Cu_2O; the yellow substance is not $CuOH$, as might be expected, but merely the oxide in a different state of subdivision. X-ray analysis shows that both varieties are Cu_2O with identical lattice dimensions.[1]

Cupric hydroxide is somewhat more stable. It is formed in the cold as a blue gelatinous precipitate which, even on warming in the liquid, is converted into the black, heavy, powdery oxide. Similar effects are

[1] Straumanis and Cirulis, *Z. anorg. Chem.*, 1935, 224, 107.

shown by thallium, and by the lower hydroxides of lead and tin : $Tl(OH)_3$ is completely dehydrated on boiling with water; $Sn(OH)_2$ is a white precipitate which passes into the red to dark brown SnO on heating with water; white $Pb(OH)_2$ is not formed when a solution of lead salt is poured into strong boiling alkali, as the yellow oxide separates out direct. Lead dioxide, PbO_2, does not appear to form a hydroxide—its content of water is entirely dependent on its colloidal nature. This oxide is produced whenever a quadrivalent hydroxide of lead might be expected, as in the hydrolysis of salts of quadrivalent lead. It is also formed by the oxidation of plumbous salts in alkaline solution, *e.g.* by the addition of hypochlorites or hypobromites to these salts. It also appears on the oxidation of a lead anode in sulphuric acid solution as in the ordinary accumulator. When red lead, Pb_3O_4 (*i.e.* $2PbO . PbO_2$), is treated with nitric acid, the plumbous portion of this compound dissolves, leaving PbO_2 as a brown powder.

Physical Properties of the Oxides.—The physical properties of oxides, especially the colour, form and density, vary with the method of preparation. When obtained at low temperatures or from solution they are not visibly crystalline, as the particles have not had a chance of rearranging themselves in the form of crystals. The same limitation affects the oxides produced from the aerosol state (*cf.* pp. 111, 143), as, for example, when they are made by burning the metal (Zn, Cd). The oxide fumes consist of minute solid particles which are unable to arrange themselves in definite crystals. Some oxides precipitated from solution have a crystalline structure (Cu_2O, SnO) and have a higher density in consequence. The form of lead monoxide is affected by the method of preparation. There are yellow and red varieties which have different X-ray lattices, showing that the difference is not merely due to a difference in the size of the particles. The yellow form is produced when single atoms of lead are oxidised, *e.g.* in the oxidation of lead vapour. The red form is made by the dehydration of the hydroxide, $3PbO, H_2O$. The carbonate also gives the red form when decomposed, and as this modification is also formed from polymerised lead salts it is probably polymerised itself. It passes into the yellow form, the transition temperature being 530°, but although the red form is the more stable at the ordinary temperature the yellow variety is not changed into it under these conditions. The red form does not pass through the yellow stage if a suitable topochemical method of formation is used, *e.g.* from solid lead compounds.

Amorphous oxides can be made crystalline by melting; crystalline alumina can be made by this method and on account of its hardness (9) it is used as an abrasive. Transformation to less reactive forms may take place by heating to temperatures below the melting points of the oxides; for example, alumina, if ignited at 1100°-1200° becomes much less hygroscopic. Even so, it is necessary in gravimetric analysis to

weigh Al_2O_3 as rapidly as possible to avoid adsorption of water vapour. Native aluminium oxide, as emery, contains iron; corundum is purer, while ruby contains traces of chromium oxide, and sapphire owes its colour to oxides of iron and titanium. These precious stones are made artificially by dropping molten alumina containing 0·2-0·3 per cent. Cr_2O_3 or 0·1-0·2 per cent. TiO_2 and a little iron oxide on to a layer of Al_2O_3; on solidification, hexagonal prismatic twins are formed. The Goldschmidt process gives alumina in scales which cannot readily be powdered. Lead monoxide (PbO, litharge, massicot), the most readily fusible of the oxides of this class, is obtained crystalline from the fused melt. Red lead forms a crystalline powder.

Amorphous oxides are often "mineralised" without actual fusion when they are heated to a high temperature. Slight volatilisation is a partial cause of the crystallisation, but the result can be obtained more easily if the oxides are heated with anhydrous magnesium chloride or borax, when they dissolve to some extent in the flux and then crystallise out again. Many oxides can be mineralised by heating with ammonium chloride and are found to be crystallised in the cooler parts of the apparatus; thus ferric oxide is mineralised at 600°—it is probably converted into chloride and then by hydrolysis or in some other way becomes oxide again. Zinc oxide can be obtained in the crystalline form by heating zinc chloride in steam. The fluorides are even better mineralising agents than the chlorides; when alumina with a little Cr_2O_3 is heated with fluorspar in a wind furnace rubies up to a millimetre in diameter are found on the cooler sides of the crucible. The transient formation of the free metal can also lead to recrystallisation of the oxide. For example, when alumina is heated with carbon to a high temperature in an atmosphere of carbon dioxide it becomes crystalline. The oxides obtained by the decomposition of the nitrate are also often crystalline (e.g. ZnO).

In many oxides (Fe_2O_3, Cr_2O_3, TiO_2, ZrO_2, Nb_2O_5, Ta_2O_5) so much heat is evolved in the transition from the amorphous to the crystalline form that the oxide glows. This may be seen if the compressed oxide is heated; loose powders give the effect less readily as the heat is more easily dissipated. The radiograms show clearly that the originally amorphous oxide has become crystalline.

The density of the oxides varies with the size of the crystals (and the presence of molecular aggregates must be assumed in oxides which are commonly described as amorphous) though in some instances the existence of definite allotropic forms is shown by crystallisation in more than one system. For the reasons indicated above there is no point in giving accurate values for the densities of these oxides. Most of them have a density approximating to 5, though aluminium oxide is lighter (about 4) and the oxides of cadmium, lead and uranium are heavier.

Many of these oxides crystallise in the regular system (NiO, MnO, UO_2, PbO, the last having also a tetragonal form), but some are hexagonal (ZnO, CdO) and a few rhombic (MnO_2). Cadmium, nickel, and probably cobalt oxide also, have the rock salt crystal structure, and are thus similar to the oxides of the alkaline earths. The triclinic tenorite, CuO, has a similar lattice, but the red zincite, ZnO, forms hexagonal crystals with a structure of the wurtzite type, like ZnS, p. 884. The oxides of univalent metals, Ag_2O and Cu_2O, have a structure related to that of the diamond: in these compounds, however, the two cells are so placed that the enclosed octahedra face in opposite directions. An attempt has been made to classify oxides according to the polarisability (= change on atom/radius of atom). When this ratio is over 15, the oxide is volatile and has a molecular lattice; between 7 and 15 are those with a glassy form, while below 7 the oxides are salt-like and have co-ordination lattices.[1]

The colour of oxides is dependent on the state of subdivision and is darker the larger the particles; the streak of the dark oxide is often the colour of the finer crystals. For example, finely divided Fe_2O_3 is red, but after strong ignition it is steel-grey (burnt oxide); Tl_2O_3 is brown in fine crystals, black in large crystals; while UO_2 is coloured brown, reddish and black, with increasing crystal size. Cadmium oxide is brown in fine, black in large crystals, while Cr_2O_3 is ordinarily grey green, but black when crystallised.

Many oxides show a deepening in colour when heated and occasionally a complete change of colour. The best known example is zinc oxide, which is white when cold and yellow when hot. The change is reversible, but the oxide becomes permanently more crystalline and does not revert to quite the original pure white colour. The colour changes on heating are summarised in the following table:

		ZnO	Cr_2O_3	NiO	MnO	Mn_3O_4
Cold	. .	White	Green	Yellowish green	Green	Reddish brown
Hot	. .	Yellow	Brown	Yellow	Yellow	Black

		In_2O_3	Tl_2O	PbO	Pb_3O_4	Cu_2O
Cold	. .	Straw yellow	Yellow	Yellow	Scarlet	Bright red
Hot	. .	Brown	Red	Red	Violet, then black	Carmine

Many of the oxides of this group are black. Besides those mentioned above, MnO_2, GeO, Co_3O_4, Ni_2O_3, Ni_3O_4, CrO, CuO, InO, V_2O_3, Mo_2O_3, FeO, Fe_3O_4 have this colour.

The colours of the oxides not yet mentioned are as follows: grey with metallic lustre, VO; dark brown to black, Mn_2O_3; dark blue to black, VO_2; deep violet blue, MoO_2; brown, WO_2, PbO_2; dark brown or red, also olive green, SnO; bright grey green, CoO; greenish brown, Pb_2O_3; white, Ga_2O_3, Al_2O_3.

The melting points of these oxides are all high. Litharge has the

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[1] Zintl and Morawietz, Z. anorg. Chem., 1938, 236-237, 372.

lowest melting point (at a red heat), while Tl_2O is somewhat similar but is still solid at 870°; CuO melts at 1064°, Al_2O_3 at 2010°, and Cr_2O_3 at about the same temperature. The boiling points are also high—that of Al_2O_3 is at 2210°; other boiling points of these oxides have not yet been accurately determined, but it is known that that of In_2O_3 lies above 1400° and ZnO does not vaporise below 1000°. In the presence of reducing gases the oxides volatilise at lower temperatures owing to formation of the free metal as an intermediate stage.

Solubility.—Only Tl_2O of all the oxides of this group shows any appreciable solubility in water. The others are practically insoluble. Those derived from the uni- or bi-valent states of metals are readily soluble in acids. The oxides of tervalent metals, on the other hand, are not easily soluble in acids, especially when crystalline, *i.e.* after ignition (Fe_2O_3, Cr_2O_3, Al_2O_3). The unignited oxides are only soluble with difficulty, and even then the solution is probably due to the formation of a colloidal solution in the first place. Hydrochloric and nitric acids do not act on the ignited oxides, but sulphuric acid, especially at a concentration of $3H_2O : 8H_2SO_4$, is effective, as it can be used at a high temperature. Fused alkali bisulphate (pyrosulphate) is even better, as the SO_3 it contains rapidly converts the oxides into sulphates. Alumina, by virtue of its acidic properties, can be dissolved by alkaline media (*cf.* p. 458).

The quadrivalent oxides of the metals, such as PbO_2 and MnO_2, do not dissolve in nitric acid, as they are not basic towards that acid; they are similarly not attacked by cold sulphuric acid, but lead dioxide forms the base of an easily hydrolysed compound, $Pb(SO_4)_2$, which appears as yellow crystals at a lead anode in the electrolysis of concentrated sulphuric acid. PbO_2 dissolves in hydrochloric acid with some formation of the corresponding tetrachloride (p. 161), which splits up subsequently with evolution of free chlorine. These oxides are powerful oxidising agents; they often catalyse the liberation of oxygen (from H_2O_2, see p. 407; from $KClO_3$ see pp. 173 and 374). Their acidic properties are dealt with in Chapter XVI.

The Hydroxides

The oxides of this group differ from those of the alkali and alkaline earth metals (except Be) in their insolubility in water. The solubilities are as follows:

BeO	Al_2O_3	ZnO	CdO	PbO	CuO	Ag_2O	MgO	
0·81	1·02	3·76	3·90	5·52	6·77	10·7	$39·2 \times 10^{-5}$	millimoles oxide per litre.
0·20	1·04	3·06	5·00	12·34	5·39	24·80	$15·8 \times 10^{-3}$	mg. oxide per litre.

Only thallous hydroxide gives a marked solubility, and this with its alkaline reaction indicates its similarity to the hydroxides of the alkali metals. It can be obtained in solution by decomposing a solution of

the sulphate with barium hydroxide or by letting the metal stand in water with free access of air.

The general appearance of these hydroxides is visibly different from those of the alkali metals. They are almost all slimy gelatinous hydrogels, and can seldom be obtained crystalline. When dried they form transparent horny masses with a conchoidal fracture. Those of aluminium and of indium form the bulkiest precipitates.

Crystalline Hydroxides.—Some of these hydroxides have, however, been prepared in a visibly crystalline form ; a few occur as such in nature—alumina as diaspore and hydrargillite, ferric hydroxide as göthite, ruby mica (both $Fe_2O_3 . H_2O$), etc. They do not usually contain much water but approximate to the ortho-formula. Similar crystalline hydroxides can be made artificially if they are formed very slowly. It is uncertain whether the slow building-up of the molecule favours crystallisation or whether basic compounds are not the first product and favour the formation of crystals topochemically (p. 142). If they are formed in the second way the supposed crystalline hydroxides are merely pseudomorphs. Crystalline aluminium hydroxide is prepared by the slow diffusion of aluminium chloride solution into one of potassium aluminate or by the decomposition of the latter solution with carbon dioxide. Zinc hydroxide can be made in a similar way and is likewise found in nature. It is also formed in electrolysis, as described below. The supposed crystalline cupric hydroxide is formed when sodium hydroxide acts on basic copper salts. Unlike the ordinary gelatinous hydrate, this blue substance is not dehydrated when heated to 100° in water, though even the former is stable in presence of sugar or certain salts (*e.g.* $MnCl_2$).

Many hydroxides, however, are only apparently amorphous. When examined by the X-ray method quite a number give indications of crystal lattices, and some even display two isomeric crystalline forms, *e.g.* $BeO . H_2O$, $ZnO . H_2O$, $Al_2O_3 . H_2O$, and $Fe_2O_3 . H_2O$ (*cf.* p. 456).

Preparation of the Hydroxides.—These compounds are made in three chief ways :

1. By treating the salts with hydroxyl ions, *i.e.* treatment with sodium, potassium or ammonium hydroxides; 2. By hydrolysis of salts of the metal without the use of other reagents ; 3. Formation in electrolysis.

The most important method is that of precipitation by bases, such as the hydroxides mentioned above. For tervalent metals, such as Al, Cr, Fe, the hydroxides may be replaced by alkali salts which are highly hydrolysed, *e.g.* sodium carbonate or potassium cyanide. All the hydroxides are formed as gels which adsorb the ions of the alkali metal and of the acid of the salts from which they are produced. It is impossible to remove these ions by prolonged washing, so that pure hydroxides cannot be obtained in this way. When the washing has reached a certain point the hydroxide passes through the filter as a sol, a phenomenon often noticed in manganese and ferric hydroxides; it is reprecipitated on falling into the washings, as these are richer in electrolytes.

This property is guarded against in gravimetric analysis by precipitating the hydroxides with ammonia in preference to sodium hydroxide; the ammonium salts can then be removed by volatilisation

in the subsequent ignition of the precipitate, while the sodium salts would remain and lead to high results. Many useful separations can be made by precipitating the hydroxides in the presence of tannin; the tannin complexes, formed by co-precipitation of the oppositely charged colloids, are very bulky but not gelatinous and can be rapidly filtered off, washed and ignited to oxides. If it is necessary to use sodium hydroxide as precipitant in order to effect a separation, the hydroxide is dissolved in acid after washing and reprecipitated with ammonia. When the hydroxide is easily dehydrated (like CuO), the salts can be washed out of the oxide formed.

If the salts of the metals are difficult to obtain, one of a lower stage of oxidation can be used and the oxidation carried out during or after the precipitation. This method is useful, for instance, in the formation of the higher oxides of nickel, cobalt and manganese. A nickelous salt is treated with sodium hydroxide and the $Ni(OH)_2$ oxidised to $Ni(OH)_3$. The most effective oxidising agent in the alkaline solution is a hypochlorite or hypobromite, so that addition of chlorine or bromine water, or treatment with bleaching powder, causes a rapid change from the light-coloured bivalent hydroxide to the black higher hydroxide of nickel, cobalt or manganese. Even the oxygen of the air converts manganous hydroxide into a higher hydroxide, a reaction similar to that observed with ferrous salts which are oxidised via ferroso-ferric to ferric, and with the hydroxides of bi- and ter-valent vanadium which are converted into the tetra-hydroxide. The lower hydroxides of nickel and cobalt are unaffected by the oxygen of the air, whereas $Cr(OH)_2$ is oxidised to $Cr(OH)_3$ even in absence of air by decomposing water with evolution of hydrogen.

Hydrogen peroxide oxidises in much the same way as atmospheric oxygen, though more rapidly. Manganese is oxidised to the $Mn(OH)_4$ stage, whereas molecular oxygen gives only the intermediate stage, Mn_3O_4, aq. Persulphates and other per-salts act in a similar way. Sodium perborate is a useful oxidising agent in such reactions, as the excess of perborate is decomposed by boiling the alkaline solution.

If a higher state of oxidation is commoner than that of the hydroxide it is desired to prepare, reduction in alkaline solution gives the lower hydroxide. Thus, $Mn(OH)_4$ can be prepared by the reduction of permanganate in alkaline solution by many reducing agents, such as alcohol, sulphites, oxalates, etc. The reduction by manganous salts is interesting; both the reduction of the MnO_4' and the oxidation of the Mn'' give quadrivalent manganese hydroxide. Chromium hydroxide is formed by the reduction of chromates, e.g. by H_2S. Cuprous oxide is produced on the reduction of complex cupric salts in presence of alkali (p. 446), and the lower hydroxide of molybdenum can be obtained by the reduction of ammonium molybdate with palladium hydride.

The second method, the hydrolysis of salts, is used in special preparations, particularly in the production of colloidal solutions of the hydroxides. Colloidal solutions can be obtained, for instance, by prolonged dialysis of the nitrates (e.g. of thorium, p. 816). When the acetates are boiled a more or less complete decomposition takes place and the acetic acid can be removed by dialysis or evaporation.

It is not possible to obtain $Mn(OH)_3$ by hydrolysis. When manganese dioxide is dissolved in concentrated sulphuric acid, $Mn_2(SO_4)_3$ is formed with evolution of oxygen, and on dilution with water $Mn(OH)_3$ is precipitated, but is acted on by the acid with formation of $Mn(OH)_4$ and $Mn^{\cdot\cdot}$. Again, when ammoniacal solutions of manganous salts are exposed to the air, it is Mn_3O_4, aq. which separates out. Hydrated manganese dioxide is obtained in the purest condition by boiling one of the lower hydroxides with nitric acid, when the bivalent manganese dissolves as nitrate.

The third method of preparation is the least important. If a zinc anode is used for the electrolysis of an alkali salt, zinc ions pass into solution and the formation of OH' ions by the electrolysed salt makes the separations of zinc hydroxide possible. It appears in the crystalline form. If a strip of zinc and one of iron are placed in an alkaline solution and the ends joined outside, the same result is obtained, and many of the other hydroxides of this group can be obtained in the same way —in particular, nickel hydroxide is formed at a nickel anode in the electrolysis of potassium hydroxide. These compounds can also be obtained by reduction at the cathode—for instance, $Cr(OH)_3$ from a chromate and $Mo(OH)_3$ from ammonium molybdate.

Colour.—The colours of the hydroxides of these metals are as follows :

$Zn^{\cdot\cdot}$, $Cd^{\cdot\cdot}$; $Mn^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Sn^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Ga^{\cdot\cdot\cdot}$, $In^{\cdot\cdot\cdot}$ white.

$V^{\cdot\cdot\cdot\cdot}$ greyish white ; $Ni^{\cdot\cdot}$, $Co^{\cdot\cdot\cdot}$, $Mo^{\cdot\cdot\cdot}$, Fe_3O_4 aq. black.

$Mn^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Tl^{\cdot\cdot\cdot}$, $U^{\cdot\cdot\cdot\cdot}$ reddish brown.

$Ge^{\cdot\cdot}$ yellow to rusty red ; $Tl^{\cdot}$, $Cr^{\cdot\cdot}$ yellow ; Mn_3O_4 aq. yellow-brown.

$V^{\cdot\cdot}$ purple red ; $Ni^{\cdot\cdot}$, $V^{\cdot\cdot\cdot}$ light green ; $Cu^{\cdot\cdot}$ blue.

$Co(OH)_2$ is blue when first precipitated by sodium hydroxide, but becomes violet and finally pink, probably as a result of hydration. $Cr(OH)_3$ appears in various colours according to its isomeric form ; they vary from greyish green to violet. The origin of these forms is the hydration isomerism discussed on p. 292. A grey blue form is produced from the various violet chromium salts when they are precipitated in dilute solution, and a green form from the green salts and from concentrated violet solutions.

Cuprous hydroxide, $Cu(OH)$, does not exist (p. 446) and $Mo(OH)_2$, $Mo(OH)_4$ and $W(OH)_4$ have not yet been prepared.

Colloidal Properties.—The general properties of these hydroxides are greatly affected by their colloidal nature. They form obvious gels when precipitated from solution and can also be obtained as clear sols, which will be considered first, as they are a limiting form of these substances.

The ter- and quadri-valent hydroxides form sols more stable than the bivalent ones. The sol of tervalent iron hydroxide has been most carefully studied ; it is readily obtained by the dialysis of ferric nitrate or of ferric chloride solution in which some ferric hydroxide has been dissolved—the hydroxide dissolves rapidly when fresh. If a solution of ferric chloride is treated with sodium hydroxide or sodium carbonate

drop by drop, the hydroxide formed redissolves on stirring until finally the solution obtained is clear dark brown in transmitted light, but with a pronounced surface colour. .(The corresponding solution of $Al(OH)_3$ is more stable, and in consequence the precipitate of the hydroxide is not at first visible in qualitative analysis, but becomes obvious when the particles have increased in size, a process accelerated by heating.) When these solutions are dialysed the bulk of the electrolytes in them can be removed, but they always require a trace of chloride ion for stability, and if the dialysis is pushed too. far the hydroxide is precipitated (*cf.* p. 101).

Another way of making the ferric hydroxide sol is by prolonged boiling of ferric acetate solution, which becomes brick-red in colour compared with the brownish-red of the sol made from the chloride. The taste is also different—the characteristic iron taste is replaced by that of free acetic acid. The particles seen in the ultramicroscope, moreover, are larger than those in the sol made from chloride, a consequence of the prolonged heating. The acetic acid can be removed by dialysis or by evaporation, the liquid lost being replaced by pure water. These colloidal solutions do not give the ordinary reactions for ferric ions, *e.g.* ferrocyanides give neither a precipitate nor a blue colour.

Colloidal solutions of $Al(OH)_3$ and $Cr(OH)_3$ can be prepared in an analogous manner. The former gives a colourless opalescent liquid, the latter is green and can be obtained only in dilute solution, although stable aluminium hydroxide sols containing 0·5 per cent. have been prepared and boiled without coagulation. The ferric hydroxide sol can be made with several per cent. of the solid in it. Naturally, much higher concentrations are possible if protective colloids are present, *e.g.* when ammonium chromate is reduced by a palladium sol in the presence of sodium lysalbinate in an atmosphere of hydrogen.

In these sols there is an optimum effect on the addition of electrolytes, and further addition does not produce further precipitation after a certain point is reached.[1] They do not altogether follow the Hardy precipitation rule (p. 101). Indeed, many different precipitants have much the same effect in equivalent concentration,[2] and the whole behaviour is more like the salting out of albumin than the usual precipitation of a suspensoid by electrolytes. These sols are intermediate in behaviour between the suspensoids and the emulsoids. The sensitiveness to sulphuric acid and sulphates is very marked, but the precipitate produced by high concentrations of hydrochloric or nitric acid is soluble in water. The usual chemical reaction leading to the formation of chloride and nitrate is almost entirely absent. In fact, the hydroxides of iron, chromium and aluminium are almost insoluble in acids on long standing, and this ageing effect is accelerated by heating the

[1] Biltz, *Ber.*, 1902, 35, 4431 ; 1904, 37, 1095.
[2] Duclaux, *J. Chim. Phys.*, 1907, 5, 29.

hydroxide, and by the presence of alkali in the case of chromium. The ageing also takes place in the colloidal solution, and usually affects the viscosity. If $Cr(OH)_3$ is peptised by alkali, it soon begins to settle out in flocks—an effect increased by heating. The hydroxides also become less soluble in acids when heated dry, short of complete dehydration, and it appears to be caused not so much by dehydration as by an increase in the size of the particles, as it takes place to the same extent when water is present. A similar result is observed with stannic acid (p. 819) and with silicic acid (p. 821).

These hydroxides do not contain a definite quantity of water. The ortho-hydrate formulae in common use, such as $Al(OH)_3$, $Sn(OH)_2$, $Mn(OH)_2$, are not in agreement with the results of analysis, as will be discussed in greater detail under silicic acid (p. 821). It would not be correct, however, to deny altogether the existence of such compounds as $Al(OH)_3$ or $AlO \cdot OH$. Some evidence is to be found in the work of Hüttig and v. Wiggenstein,[1] who noticed that freshly precipitated aluminium hydroxide forms a typical gel, with no crystal structure apparent to X-ray analysis. On ageing the precipitate gives a radiogram due to $Al(OH)_3$, as in the mineral hydrargillite. By removing the water by heat this passes without intermediate stages to $AlO \cdot OH$ (böhnite, of the same composition as bauxite), which once again has a completely unorientated structure and on further dehydration gives no further indications of definite hydrates. If, however, the hydrate is allowed to age spontaneously the loss of water follows a different course, as may be seen from dehydration curves. Thus by proceeding along different paths of dehydration it is possible to obtain products of the same chemical composition but with a different chemical structure. Hydrargillite can also be obtained by decomposing alkali aluminates in various ways, as well as a metastable form of the same composition, bayerite (Fricke).[2] Isomers of this sort have been studied by W. Biltz and G. A. Lehrer[3] who assume an isomerism of the type: $[Al_2O_3, H_2O]2H_2O$ and $[Al_2O_3, 3H_2O]$. The investigation of such systems has received a stimulus from the adoption of Willstätter's method of washing the precipitates with acetone. The difficulty of dehydrating such colloidal conglomerates depends on the fact that the vapour pressure due to the water in the capillaries of the gels is much diminished; but if a medium is used for washing which is miscible with water, no pure water surface is formed and the pressure approaches normal. Rehydration also follows courses which depend on the previous history of the sample of gel and the method of extraction and addition of the water. Hydrates which have only been partly dehydrated take up water rapidly in the air, but after complete dehydration much less water is so absorbed. The equilibrium set up

[1] *Z. anorg. Chem.*, 1928, **171**, 323.   [2] *Ibid.*, 1928, **175**, 249.
[3] *Ibid.*, 1928, **172**, 292.

with the water vapour of the air varies with different samples of the same hydrate. It is very difficult to dehydrate these hydroxides completely and $Cr(OH)_3$ retains traces of water even after roasting at quite high temperatures. On the other hand, some of these hydroxides are lower in water content than is required by the ortho-formula, even when they are dried at room temperature; thus stannous hydroxide never contains more water than corresponds to the formula $(SnO)_2,H_2O$, and the same is true of plumbous hydroxide. These hydroxides are easily dehydrated and pass into the oxide (cf. p. 446). Precipitated Cu_2O, PbO, SnO, Tl_2O_3 and $TlOH$ are completely dehydrated in vacuo at room temperature.

The striking tendency of these gelatinous hydroxides to adsorb substances from solution makes it difficult to purify them. An interesting practical application of this property is the use of ferric hydroxide as an antidote in arsenical poisoning. It was originally supposed that a definite basic ferric arsenite was formed, but Biltz showed[1] that the distribution of the arsenic between the hydroxide and the solution gave a curve typical of adsorption. A similar example of excessive adsorption is that of phosphoric acid by stannic acid, but it seems probable that the forces operating in these excessive adsorptions are more "chemical" than usual, though Michaelis holds that all adsorption has a chemical basis.

Classification of Hydroxides.—The chemistry of the hydrated oxides of the less electropositive metals forms one of the most difficult chapters of inorganic chemistry. Their properties, structure, formation and ageing place them outside the general lines of method and theory of pure chemistry or even of colloid chemistry and involve all sorts of questions of thermo-chemistry, thermodynamics and of optics. Hüttig suggests a first subdivision into crystalline and amorphous hydroxides, although in many respects the other differences are few. The crystalline ones can be detected by X-ray analysis, when they show definite interference bands, while the amorphous ones give only a general darkening. Two kinds of crystalline forms may be characterised—those with a distinctive lattice of their own and those which have the lattice of the parent salt. In the latter, water molecules have entered the positions in the lattice previously occupied by the acid radicals of the salts from which the hydroxides were made. The water is thus parasitic in a strange lattice and such structures are not stable in the thermodynamic sense.

It is more difficult to be certain of the amorphous forms owing to the effects of ageing. The first products are usually amorphous, the final stages crystalline; and the change proceeds through a continuous series of intermediate forms, in which the content of free energy continuously diminishes. It can thus be seen that an amorphous hydrate

[1] *Ber.*, 1904, **37**, 3138.

may be converted into another of different water content, which then reverts to a crystalline form of the first.[1] The relations become more complex than this because several modifications of the same composition exist. Further, the normal ageing curves of hydroxides of the same composition but made in different ways may intersect. For instance, hydrargillite and bayerite both have the composition $Al_2O_3 . 3H_2O$ and are related to diaspore and böhnite; göthite and ruby mica are examples from another series ($Fe_2O_3 . H_2O$). Intermediate stages, however, are obtained from the same dehydration series between bayerite and böhnite and between bayerite and hydrargillite. These substances can be characterised because they are crystalline; others which are amorphous are more difficult to identify. The pressure of water vapour does not serve to indicate the crystalline hydroxides, as equilibrium is only slowly established and is frequently irreversible. Other physicochemical methods of establishing individuality also fail, as the amorphous hydroxides are too readily decomposed. At present there is no experimental criterion for finding when an amorphous gel is really an individual substance.[2]

Chemical Properties.—Except for the aged hydroxides of tervalent metals all the hydroxides in this group dissolve in acids to give salts, and by the solution of hydroxides in sulphuric acid, salts which are normally unstable can be obtained. Thus manganic sulphate is formed when the higher manganese hydroxide is dissolved in this acid, and it is sometimes assumed that a solution of nickelic sulphate (pink) is formed by digesting $Ni(OH)_3$ in $KHSO_4$ solution; $Ni_2O_3 , 2H_2O$ or Ni_2O_3 , H_2O with HCl give $NiCl_2$ and Cl_2. Many of these hydroxides also dissolve in ammonia and in organic amines, notably the hydroxides of nickel, copper, zinc and cadmium. Chromium hydroxide also dissolves in ammonia, but very slowly, and $Co(OH)_2$ only in concentrated solutions. The solution of these hydroxides is a consequence of the formation of complex ammines, as is obvious from the characteristic colours produced—Ni, blue; Cu, deep blue; Cr, violet, etc. Gallium hydroxide, $Ga(OH)_3$, is soluble in ammonia only when freshly precipitated, and in this case it is probably a question of a colloidal solution rather than the formation of an ammine. None of these ammines have been isolated in the solid state, but some of them have important practical applications. The ammine of cupric hydroxide (Schweizer's reagent) has the astounding property of dissolving cellulose, which leads to one process for the manufacture of artificial silk. The dark blue solution is obtained when copper is exposed to the joint action of air and ammonia, when oxidation takes place; the liquid formed in this way always contains appreciable quantities of nitrites. Other substances besides ammonia also form complexes with

[1] Haber, *Naturwiss.*, 1925, 13, 1011.
[2] Cf. *Z. angew. Chem.*, 1929, 42, 886.

hydroxides and cause them to go into solution, although, again, the complexes have not been isolated. One of the most striking examples is the effect of organic substances containing OH groups, such as glycerin, cane sugar and oxyacids like tartaric acids, which form internal complexes (p. 343). These substances are so stable that the ordinary reactions of the ions of the metal in them are lacking. Thus solutions of aluminium, chromium, vanadic and cupric salts, to which tartaric acid has been added, are not precipitated by sodium hydroxide or ammonium sulphide. This property is useful in analysis, as clear alkaline solutions of these metals can be obtained in this way. The best known example is Fehling's solution, which contains a cupric salt, a tartrate and sodium hydroxide, and is used in testing for reducing substances which precipitate cuprous oxide (p. 445). A few of these hydroxides are also soluble in alkali carbonates; e.g. $Cu(OH)_2$ dissolves in K_2CO_3 or $NaHCO_3$ solutions, owing to the formation of complex carbonates; this reaction occurs only with bivalent metals—the tervalent ones do not give normal carbonates.

The solution of stannous hydroxide in alkalis—formerly regarded as a stannite solution—has some remarkable properties. It undergoes autoxidation and reduction when a part of the tin separates out as a dark precipitate of the metal, while the rest is oxidised to stannate. It is therefore a powerful reducing agent and liberates lead, bismuth, antimony, etc., from alkaline solutions of their hydroxides, while cupric salts are reduced to Cu_2O.

Acidic Properties.—Many of these hydroxides are soluble in excess of sodium or potassium hydroxide. This has been commonly attributed to the formation of salts, the hydroxides behaving as amphoteric substances and giving either OH′ or H˙ ions according to the conditions of experiment. In presence of strong alkalis they were supposed to behave as acids, thus:

$$Al(OH)_3 + 3NaOH \longrightarrow Na_3AlO_3 + 3H_2O \text{ or } Al(OH)_3 + NaOH \longrightarrow$$
$$NaAlO_2 + 2H_2O; \quad Zn(OH)_2 + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O.$$
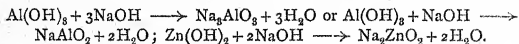
The bivalent hydroxides of lead and tin, as well as both hydroxides of gallium, have the same property, while $Ge(OH)_2$ is more difficultly soluble, though germanites, e.g. Na_2GeO_2, have been obtained. Excess of KOH dissolves $In(OH)_3$ in the first place, but it is reprecipitated after a time; $Cr(OH)_3$ remains in solution for a time in the cold, while $Cu(OH)_2$ only dissolves for a short time in very strong alkali, giving a deep blue sol. The other hydroxides of this group are insoluble in alkalis. The compounds formed are known as aluminates, zincates, plumbites, stannites, etc., but it is probable that the solution of the hydroxide is not so much a matter of compound formation as of peptisation of the hydroxide to form a sol. The solutions of aluminate, chromite, etc., are almost completely hydrolysed

unless a great excess of alkali is present, and the conductivity of the solutions is equal to that of a plain solution of the alkali. The heavy metal portion of these supposed compounds does not diffuse through parchment paper, so that it would appear to be entirely colloidal and not ionic or in ordinary solution. The concentration of hydroxyl ions in these solutions is that of the alkali they contain. The formation of at least some aluminate is demonstrated by its isolation from very concentrated solutions (see below), but in dilute solutions the reaction of the hydroxide with the alkali is an unimportant effect compared with the formation of the colloidal solution.

Compounds of the Hydroxides with Bases.—Compounds which are crystalline, of constant composition, and can be regarded as salts, can only in fact be isolated from the solutions of zincates and aluminates. They are precipitated when the solutions are treated with alcohol; the aluminium salt also crystallises spontaneously from very concentrated solutions. Of the zincates, only the potassium and sodium salts are known; they have various types of formulae, of which the most important are K_2ZnO_2 and $KHZnO_2$. The aluminates have a still greater variety in their composition, as indicated by the formulae $4MO,Al_2O_3$, aq.; $3MO,Al_2O_3$, aq.; MO,Al_2O_3. Aluminates of the alkalis and of the alkaline earths are known. They are hydrolysed by water, but this is only apparent after some time, as the aluminium hydroxide remains in colloidal solution. The most notable of the solid adsorption compounds is the "calcium manganite" formed in the Weldon process for the regeneration of the manganese dioxide used for the manufacture of chlorine; the solutions containing manganese chloride are made alkaline with lime and oxidised by blowing in air.

On the other hand, when the oxides are melted together or otherwise caused to combine in the absence of water, well-crystallised compounds are formed, in which one oxide forms the positive and the other the negative part of what appears to be a true salt. The best known of these compounds are the spinels, a series of minerals crystallising in the regular system and analogous in structure to the original spinel, $MgO.Al_2O_3$. The magnesium may be replaced by many other bivalent metals and the aluminium by tervalent ones. Thénard's blue, the bright blue mass obtained when Al_2O_3 is heated with cobalt nitrate, probably belongs to this class, and serves as a useful test for aluminium. Artificial spinels can be made by heating the oxides with a mineraliser such as borax, or even without its use if a very high temperature is attained. The component oxides may even be produced during the heating process, as when chromium spinels are made by heating the chromates of the heavy metals, when the Cr_2O_3 is first formed by reduction. Compounds of composition different from the usual formula $MO.M_2O_3$ are also known. Many of these salts formed from two

metallic oxides are found as minerals in nature; for example, chrome iron ore, which is iron chromite, and franklinite, a zinc ferrite, $ZnO.Fe_2O_3$. Owing to the high temperature of formation, the spinels are resistant to acids, but fusion with alkalis removes the more acidic oxide (e.g. the Al_2O_3). The calcium ferrites CaO,Fe_2O_3 and $2CaO,Fe_2O_3$ as well as the calcium and cadmium indates, CaO,In_2O_3 and CdO,In_2O_3, have been prepared in the dry way.

It may be anticipated that the oxides of quadrivalent metals will also form compounds with those of bivalent metals, and besides the stannates (see p. 831) a number of plumbates exist. They have the general formulae $MO.PbO_2$ and $2MO.PbO_2$, and the acidic nature of the PbO_2 is indicated by the fact that they are not completely hydrolysed by water, and can even be recrystallised from strongly alkaline solutions. The colourless, water-soluble plumbates of the alkalis can be prepared in the wet way, but those of the alkaline earths are best made by fusing the mixture of oxides together. The application of calcium plumbate, Ca_2PbO_4, to the preparation of oxygen from the air has already been mentioned; this compound can be made by fusing lime and lead oxide in the air, or even by the oxidation of an aqueous suspension of the two oxides by atmospheric oxygen. Compounds of $Mn(OH)_2$ with lime formed in a similar way appear to be adsorption mixtures. If manganese dioxide is fused with caustic alkalis in absence of air it decomposes into Mn_2O_3 and MnO_3, when the latter gives manganate, but no manganite is produced.

Very often the different oxides of the same metal form condensation products resembling salts. Thus red lead, Pb_3O_4, may be regarded as plumbous plumbate $\overset{II}{Pb}\diagdown\!\!\!\overset{O}{\diagup}\overset{IV}{Pb}\diagdown\!\!\!\overset{O}{\diagup}\overset{II}{Pb}$, and in the same way $Fe_3O_4 = FeO,Fe_2O_3$; $Mn_3O_4 = MnO,Mn_2O_3$; $Co_3O_4 = CoO,Co_2O_3$; $Pb_2O_3 = PbO,PbO_2$. These oxides are discussed on p. 443. Mn_2O_3 must be regarded as the true oxide of tervalent manganese for it dissolves in cold concentrated hydrochloric acid to give a solution of the corresponding chloride; but its reaction with hot concentrated nitric acid to give $Mn(NO_3)_2$ and MnO_2 suggests a second possible formulation, MnO,MnO_2.

Peroxide Hydrates.—These compounds are known for zinc and cadmium and resemble the corresponding compounds of the alkaline earths (p. 423); they are prepared in the same way as the latter— by the action of hydrogen peroxide on the hydroxides, but only $Cd_4O_7.2H_2O$ and $3CdO.H_2O_2$ have yet been isolated in a state of purity. Copper also gives a peroxide hydrate which is brown in colour, and is formed when hydrogen peroxide acts on copper hydroxide at $0°$. It probably has the constitution $HOCu.O.O.CuOH$, for it is immediately decomposed by acids, with formation of hydrogen peroxide and a cupric salt, and it does not differ from hydrogen peroxide in its

oxidising action. It is crystalline and gives off oxygen even when warmed to room temperature.

Another copper peroxide, inaccurately termed cupric acid, is formed by the interaction of cupric oxide and bleaching powder in the presence of alkali. It is a yellow precipitate which has not been thoroughly investigated, but which probably has the composition Cu_2O_3 aq. The same sort of compound is formed when a copper anode is oxidised in potassium hydroxide solution, giving an orange-yellow precipitate. Peroxides are often formed when metals are oxidised at the anode; the best known example is the production of a nickel hydroxide containing more oxygen than Ni_2O_3, which is probably a solid solution of hydrated Ni_2O_3 in NiO_2. This compound is employed in the Edison accumulator.

Oxygen Compounds of the Noble Metals

Affinity of the Noble Metals for Oxygen.—The oxides to be considered here are the following:

Ag_2O	Hg_2O	Au_2O			Rh_2O			
	HgO	AuO	PdO	RuO	RhO	PtO	IrO	OsO
		Au_2O_3		Ru_2O_5	Rh_2O_3		Ir_2O_3	Os_2O
			PdO_2	RuO_2	RhO_2	PtO_2	IrO_2	OsO_2
				RuO_4	RhO_3	PtO_3	IrO_3	OsO_4

The oxides OsO_3, RuO_3 and Ru_2O_7 do not exist in the free state, but only as salts. The osmates, ruthenates and perruthenates are intensely coloured. IrO_3, which has not been obtained pure, corresponds to such substances as $K_2Ir_2O_7$ and K_4IrO_5, H_2O.

Although these metals are classified as noble by the electrometric method, they differ considerably in their affinity for oxygen; only a few of them are not attacked by oxygen, at any rate when finely divided —these include gold, platinum and silver. The last dissolves large quantities of oxygen when fused but gives it up on cooling with the well-known spitting of silver. This appears to be due to the formation of Ag_2O, and this oxide can be obtained direct in small quantities from the finely divided metal at 200°. Mercury, on the other hand, can be completely converted into oxide on heating in air, though it gives up its oxygen again on a slight rise of temperature. At the other end of the scale are some of the platinum metals, which are not only completely converted into oxide on roasting in the air, but retain the oxygen at very high temperatures. Ruthenium, rhodium, and especially osmium, behave in this way; the last ignites spontaneously in the air when finely divided and burns to OsO_4.

Once the oxides are formed, silver, gold and platinum retain their oxygen with some tenacity. Silver oxide, according to calculations, should be a very labile substance and have an enormous dissociation

pressure at room temperature; in practice its decomposition only begins at 200° and becomes marked at 250°. All the other oxides of this group, however, have a positive heat of formation, and in some cases it has been possible to measure the dissociation pressure. For example :

Ag_2O	Temp.	302°	325°	445°
	Press. of O_2	20·5	32	207 atm.
HgO	Temp.	400°	500°	
	Press. of O_2	231	798 mm.	

The results for the oxides of platinum are interesting. The monoxide is produced at 510°-560° from platinum black and oxygen. The higher oxides do not pass direct to the lower ones, but solid solutions of the decomposed oxide in the undecomposed portion are formed, so that no definite transition point can be detected. It is curious that the dissociation pressure of the Pt_2O_3 and PtO mixture is higher than that of PtO_2, so that these intermediate oxides break down on heating[1] into metallic platinum and the higher oxide PtO_2. In a similar manner RuO_2 gives the metal and tetroxide at 1000°, and Hg_2O decomposes into HgO and free mercury at the ordinary temperature, especially when exposed to light.

Light also decomposes Ag_2O and Au_2O_3; the silver oxide gives a substance which retains its oxygen very loosely and on treatment with halogen acids yields photo-halides. Silver oxide is readily reduced by traces of organic matter at low temperature, e.g. during drying.[2] Catalytic action is very important in the reduction of these oxides; for example, the thermal decomposition of silver oxide takes place at a rate which increases with time at first and only slows down towards the end of the reaction owing to the presence of the metallic silver formed. The effect of the silver can be imitated by the addition of platinum or pyrolusite. Hydrogen reduces these oxides fairly readily, some of them with a great evolution of heat; thus PtO glows when hydrogen is passed over it, PdO takes fire in hydrogen at room temperature, and Au_2O_3 burns with a brilliant flame in warm hydrogen.

Preparation.—The oxides of silver, mercury, univalent gold and bivalent iridium form no hydrates, so that the oxides are obtained direct when solutions of the corresponding salts are precipitated with sodium or potassium hydroxides. The oxides retain small quantities of water, and it is possible that chemical combination of water with aurous oxide may take place, though even in this instance the water is lost on heating to 200° without the oxide being decomposed. The other oxides, such as Au_2O_3, PtO_2, PtO, etc., are made by dehydrating the hydroxides, an operation which is often accompanied by loss of oxygen from the

[1] Wöhler and Frey, Z. Elektrochem., 1909, 15, 141.
[2] Riley and Baker, J. Chem. Soc., 1926, 2510.

oxide, *e.g.* in PtO$_2$. Sometimes the salts of the metals can be fused with sodium carbonate, and the oxides recovered by leaching out the soluble alkali compounds; this method is particularly useful in the preparation of the lower oxides, such as RuO, PdO, OsO, but it can also be employed for Ir$_2$O$_3$, Os$_2$O$_3$, OsO$_2$ and some others. Roasting or fusing the metal in a stream of oxygen is also a useful method of preparing these oxides, and besides HgO, a well-known example, RhO can also be made in this way. Further, Ru$_2$O$_3$ is obtained by heating the metal in air at a moderate temperature, RuO$_2$ at a higher temperature, in a stream of oxygen. If RuO$_4$ is heated slightly above 100° it breaks down into black, non-volatile lower oxides. OsO$_4$ is obtained by heating metallic osmium or its compounds in oxygen.

It is sometimes necessary to use more powerful oxidising agents than free oxygen when higher oxides are required. Thus Rh$_2$O$_3$ is made by fusing rhodium with barium peroxide, RhO$_2$ and OsO$_4$ by heating the metal with caustic alkali and potassium nitrate or sodium peroxide; this method naturally gives salts when the oxide has acidic properties. Thus ruthenium gives potassium ruthenate K$_2$RuO$_4$, a salt of the unknown oxide RuO$_3$. The oxide or hydroxide is, however, commonly obtained when these salts are acidified, and auric hydroxide is formed on treating Ba(AuO$_2$)$_2$ with nitric acid, and platinic anhydride, PtO$_3$, by acidifying the salt K$_2$O,3PtO$_3$ with acetic acid. The "perosmic anhydride," OsO$_4$, obtained when an osmate like K$_2$OsO$_4$ is acidified, is the result of a decomposition similar to that of manganate into permanganate and manganese dioxide. The salts of the acid H$_2$OsO$_3$ undergo a similar decomposition on acidification, giving OsO$_4$ and Os(OH)$_4$. The higher oxides of osmium and ruthenium are easily isolated owing to their volatility. Although these oxides are formed to some extent by heating the metal in oxygen, they are more readily prepared by oxidising the metal in solution—the osmium with *aqua regia* and the ruthenium with chlorine in alkaline solution—the volatile oxide being distilled off from the solution. This process applied to rhodium gives RhO$_2$,2H$_2$O as a green non-volatile powder, but it decomposes when dehydrated; RhO$_3$ is formed simultaneously and decomposes to Rh$_2$O if heated above 900°.

When hydroxides exist they are prepared by the usual method of treating the salts with alkali hydroxide or carbonate. Au(OH)$_3$, Pt(OH)$_2$, Pt(OH)$_3$, Pt(OH)$_4$, Ru(OH)$_3$, RuO$_2$.5H$_2$O, Rh(OH)$_3$, Pd(OH)$_2$, Ir(OH)$_3$, Os(OH)$_3$, Os(OH)$_4$, etc., can be obtained in this way. Either simple salts or complex compounds may be used; *e.g.* Na$_3$RhCl$_6$, K$_2$PtCl$_4$, K$_2$PtCl$_6$. Some of the hydroxides can also be obtained by the hydrolysis of salts, and the hydroxides of AuO and Au$_2$O$_3$ are obtained by the addition of water to the sulphates.

Colour, etc.—The colour of these oxides and hydroxides is notably affected by the dispersity of the particles; this is most familiar in

mercuric oxide, an example discussed below. In some of the other oxides differences of constitution may also be operative in giving these colour changes. Thus $Au(OH)_3$ is goldfinch yellow to olive green when first precipitated, but becomes rusty yellow to ochre brown on standing, while when dried it is dark brown. It is probable that this behaviour is due to the same causes as that of the hydrate of PtO_2, which is white when first precipitated, but becomes ochre brown when boiled in the solution, and on drying turns browner and finally black. This hydroxide is obtained by dissolving $PtCl_4$ in concentrated caustic soda and then precipitating with acetic acid, and, according to Bellucci,[1] it is a hexahydroxy-platinic acid $[Pt(OH)_6]H_2$. On heating, it passes into the acid $\left[Pt\dfrac{O_4}{H_2}\right]H_2$, which is also obtained when $PtCl_4$ is heated to 180° with sodium hydroxide in a sealed tube. The originally coloured solution then becomes colourless, and a coloured precipitate settles out. It is, however, fairly useless to attempt to give a constitutional interpretation to the colour changes which are observed in the drying of gels.

The oxides of this group are mostly brown, grey or black. Apart from mercuric oxide and the platinum and gold hydroxides mentioned above, only the tetroxides have light colours. OsO_4 is a white crystalline mass which gives colourless shiny needles on sublimation; RuO_4 forms golden crystals, and even the vapour is yellow. Au_2O is violet while still wet, but becomes greyer on drying. $RhO_2.2H_2O$ is green, $Ir(OH)_3$ yellowish green; while Hg_2O, AuO, PtO_2, PdO_2, IrO and $Rh(OH)_3$ are black powders. The last forms a black jelly when wet, but on drying it becomes grey with a metallic lustre. The dark brown compounds include $Pt(OH)_2$, Os_2O_3, $Os(OH)_4$ (gelatinous), Ag_2O, Au_2O_3, $Ru(OH)_3$, $RuO_2.5H_2O$ (gelatinous). $Pt(OH)_3$ is brown, but becomes black on loss of water. $Pd(OH)_2$ is dark brown, PtO_3 and $Os(OH)_3$ are reddish brown, while RhO_2 is also brown. PtO and RhO are grey, RuO, OsO and OsO_2 are grey black; Ru_2O_3, Ir_2O_3 and PdO are dark blue, while RuO_2, which is isomorphous with SnO_2, is violet with a metallic lustre.

The colour changes in mercuric oxide are very striking. When first precipitated with caustic alkalis it is egg-yellow, changing to red on heating, and not reverting to the yellow colour on cooling again. The oxide obtained by heating mercury in oxygen is red, and the yellow form when kept in glass containers becomes red where exposed to light after some years. This colour change is not due to a different allotropic form, but merely to a difference in size of the crystals. The yellow form is also more soluble in water than the red, a fact which can be accounted for by the smaller size of the yellow particles. The solubility of the red variety can be increased by mere grinding. Both forms lose their colour

completely at very low temperatures, but regain it on return to ordinary conditions (*cf.* p. 449).

Solubility.—The yellow mercuric oxide is appreciably soluble in water; one part dissolves in 19,300 parts of water at 25° and in 2400 parts at the boiling point. The solution, however, has only very weak basic properties, for of the slight quantity dissolved only 2 per cent. is dissociated, giving it the low conductivity of $2 \cdot 1 \times 10^{-6}$ mhos. Silver oxide, on the other hand, is a strong base; its solubility is not very high ($2 \cdot 16 \times 10^{-4}$ moles per litre at 25°), but of the oxide in solution some 66 per cent. is dissociated at 20°. In consequence, litmus is turned blue by the solution of the oxide, and solutions of the salts of silver are not hydrolysed like those of the other oxides of this group. Further, silver oxide precipitates the hydroxides of Zn, Cu, Hg, Bi, Fe, Al, Cr and Co from solutions of their salts, while those of Cd, Pb and Mn are only partly precipitated. Conversely, when hydroxides of Zn, Cd, Pb or Mn are added to a solution of a silver salt they become brown, showing that some Ag_2O is precipitated. Ag_2O is also used in the replacement of halogens by hydroxyl groups in organic compounds.

The other hydroxides in this group are all practically insoluble in water, but they give colloidal solutions when they are formed in the presence of protective colloids, for which purpose the products of decomposition of albumin are particularly useful. The colloidal solutions of silver and of mercury oxides are applied in medicine, as they are readily reduced to the metal. Freshly precipitated silver oxide is peptised by potassium hydroxide without the assistance of protective colloids, but the peptising action of alkalis is not so common in this group of hydroxides as in those of the baser metals. In fact, as a rule, the alkali dissolves the hydroxide only when there is a chance of salt formation; for example, $Au(OH)_3$ is difficultly soluble in cold KOH, but, on boiling, a soluble aurate is produced. PtO_2 similarly gives salts of the acid $[Pt(OH)_6]H_2$; $RuO_2 . 5H_2O$ dissolves to a yellow solution; RuO_4 and OsO_4 dissolve in water, but do not give salts if alkali is present (*cf.* p. 466).

These oxides do not always dissolve in the acids with which they form salts. Thus $Au(OH)_3$ dissolves only in concentrated nitric acid, and is precipitated owing to hydrolysis when the solution is diluted. $Pt(OH)_2$ is also only soluble in concentrated acids when freshly precipitated. PdO, RhO_2, OsO, OsO_2 and Ru_2O_3 are insoluble in acids, while $Os(OH)_3$ and $Ru(OH)_3$ are soluble, and the behaviour of PtO_2 depends on its previous treatment.

The Tetroxides.—Ruthenium dioxide, RuO_2, is volatile at high temperatures without decomposition, giving violet crystals with a metallic lustre, but volatility is most characteristic of the tetroxides of osmium and ruthenium, OsO_4 and RuO_4, which can be distilled at

2 G

low temperatures. OsO_4, obtained by burning osmium in oxygen, forms colourless transparent crystals melting at $40.7°$ to a liquid which boils at $131.2°$; even at room temperature the vapour pressure is so high that the substance has a very powerful smell resembling that of chlorine. This smell can be detected at as low a concentration of OsO_4 as 2×10^{-5} mg. per c.c., a limit which is slightly lower than that for iodoform (6×10^{-5} mg. per c.c.). The vapour is tasteless, but has a very pronounced and painful action on the eyes, resulting in partial blindness. The transparent orange needles of RuO_4 melt at $25.6°$ and are also very volatile. They have a strong smell like ozone, and explode on heating. The low temperature of vaporisation in these compounds is due to the large quantity of oxygen they contain, an effect which is also met with in the higher oxide of manganese (p. 474). It is very curious that these compounds are not acid anhydrides; they certainly dissolve in alkalis, but no salts are formed and they dissolve just as well in water alone (RuO_4 only when not previously melted; 100 c.c. water dissolves 6.5 g. OsO_4 at $20°$). Further, the solution retains the intense smell of the oxide, and the concentration of hydroxyl ions in the alkali is unaltered by the solution of these substances. The remarkable solubility of OsO_4 in carbon disulphide (250 g. in 100 g. CS_2 at $20°$) also indicates that it is a non-electrolyte. As may be expected, their aqueous solutions do not redden litmus; but it is difficult to see why a higher oxide should not have acidic properties when the lower oxides of the same metal, $e.g.$ OsO_3, already have this tendency, forming osmates, M_2OsO_4. Tschugaev[1] claimed to have prepared yellow and brown salts of perosmic acid. According to Krauss and Wilken,[2] these have the formula $OsO_4 . 2M^IOH$, and oxyfluorides of the type $OsO_4 . 2M^IF$ are stated to exist. D. Yost and R. White[3] found that the partition coefficient of OsO_4 between CCl_4 and water is affected by the presence of alkali. The fact remains that this supposed perosmic acid is certainly very weak, though one might expect an acid of such a high degree of oxidation to be strong. It is possible that the "salts" are not true salts but addition compounds of another kind. OsO_4 can certainly form complex compounds with weak organic bases (cf. also the problem of OsF_8, p. 356).

These tetroxides are powerful oxidising agents; OsO_4 is stable on keeping, but RuO_4 decomposes especially in solution with liberation of oxygen, and formation of lower oxides. The reduction of OsO_4 gives the strongly coloured $Os(OH)_4$ so the tetroxide is used for staining fats in microscopical work. Ruthenium tetroxide, RuO_4, decomposes only to the septavalent stage, giving salts of the type $KRuO_4$ in the presence of alkali, which correspond to the unknown oxide Ru_2O_7. The black crystals of this salt are also obtained when the orange

[1] Compt. rend., 1918, 167, 162 ; Z. anorg. Chem., 1928, 172, 217.
[2] Z. anorg. Chem., 1925, 145, 151.   [3] J. Amer. Chem. Soc., 1928, 50, 81.

ruthenate K_2RuO_4, corresponding to the manganate, is oxidised with chlorine.

Aurates, Osmates, Platinates.—These salts, in which the metallic oxide acts as an acid anhydride, are given only by ruthenium, osmium, platinum and gold. The osmates (*e.g.* $K_2OsO_4 . 2H_2O$) are obtained when an alkaline solution of osmium tetroxide is reduced with a few drops of alcohol. They form dark red crystals which revert to OsO_4 in damp air, while on reduction $Os(OH)_4$ is formed. The indigo-blue compound $KOsO_3$ is obtained when $K(OsO_3N)$ is heated (p. 469). The aurates $MAuO_2$ can be made by the direct solution of $Au(OH)_3$ in concentrated alkali; the yellow solution is highly hydrolysed but gives pale yellow needles of composition $KAuO_2 . 3H_2O$ on evaporation. The barium salt, $Ba(AuO_2)_2 . 5H_2O$, forms small sparingly soluble green crystals and the calcium salt dissolves if excess of a calcium salt is used as precipitant.

Platinum gives several series of salts of this kind. The salts of hexahydroxy-platinic acid (*e.g.* $[Pt(OH)_6]K_2$) are formed by the direct interaction of the acid and alkali; they are yellow and isomorphous with the stannates $[Sn(OH)_6]M_2$. The alkali salts are soluble, the barium salt sparingly soluble. A salt containing more oxygen, $K_2O . 3PtO_3$, is obtained by anodic oxidation of the alkali platinates; on addition of acetic acid, PtO_3 (p. 463) is liberated, which gives off oxygen on standing and liberates chlorine from hydrochloric acid.

Ammines of the Oxides of the Noble Metals.—These oxides give two kinds of compounds with ammonia. The first class are highly explosive and include fulminating silver and gold, together with less explosive compounds of platinum and mercury, while the second class possess this property in a much lesser degree or not at all, and are more like normal ammines.

Among the explosive compounds, *fulminating silver* is the most violent. It is formed by the action of ammonia on silver oxide or by adding potassium hydroxide to an ammoniacal solution of a silver salt. It is a black powder which explodes with violence in the liquid in which it is formed if the slightest stirring is used. It is soluble in aqueous ammonia and the solution has strong basic properties—it is more alkaline than $Ba(OH)_2$. It is therefore highly probable that a complex of the type $[Ag(NH_3)_x]OH$ is present, for the silver hydroxide is itself a strong base, and the formation of a complex increases this tendency (*cf.* p. 617).

The analogous *fulminating gold* has been the subject of more detailed investigation.[1] This is also obtained by the action of ammonia on auric salts, but the brown precipitate is not $2Au(OH)_3 . 3NH_3$, as it contains chlorine. This is due to the presence of the compound $[Cl(NH_2)Au]_2NH$, but on washing with ammonia the explosiveness is increased, owing to the hydrolysis of this substance. On shaking with a solution of a chloride, the chlorine compound is once again formed from the product of hydrolysis—there is, in fact, a definite equilibrium between the substance containing chlorine and the one which does not. The non-explosive diamido-aurichloride, $AuCl(NH_2)_2$, is the sole product

[1] Weitz, *Ann.*, 1915, 410, 117.

from strong solutions of ammonium chloride. When the ammine $2Au(OH)_3 . 3NH_3$ is heated with water the more explosive $Au_2O_3 . 2NH_3$ is formed; by dry heating the equally explosive $Au_2O_3 . 3NH_3$ is obtained, which eventually passes into the aurous compound $3Au_2O . 4NH_3$—which also explodes.

The explosiveness of these compounds is probably due to the tendency of the hydrogen and oxygen to combine being greater than the attraction of the nitrogen and the metal for these elements; the effect is similar to that observed in ammonium nitrite (p. 178), though there the oxygen is more firmly attached to the nitrogen than it is to the metal in these fulminating compounds. In fact, all metal oxides of low heat of formation give explosive ammines when they form any at all; thus a fulminating platinum can be obtained by the action of caustic alkalis on ammonium platinichloride, and explosive compounds of mercury are also known, the most important being Millon's base (p. 627). This can be considered an ammine, $2HgO . NH_3$, although other views of its structure are tenable. It is not very explosive, but if it is dehydrated or if gaseous ammonia is passed over HgO at a higher temperature, a more explosive brown powder is formed, which is supposed to have the formula $(NHg_2)_2O$; if this is really free from hydrogen the above explanation of the explosiveness does not hold good.

It is remarkable that there are platinum ammines which are only slightly or not at all explosive. It is possible that in these the nitrogen atom is more firmly attached to the metal, and the decomposition takes place less rapidly.

For example, the compound $[Pt(NH_3)_4](OH)_2$ is formed as soluble white needles, which are not explosive, when the sulphate $[Pt(NH_3)_4]SO_4$ is treated with baryta water. In the same way $[Pt(NH_3)_2(SO_4)]$ gives $[Pt(NH_3)_2(OH)_2]$, which can be dehydrated to the insoluble but inexplosive oxide $[Pt(NH_3)_2O]$. Similar compounds can be obtained from quadrivalent platinum, e.g. $[Pt(NH_3)_4](OH)_6$, white crystals scarcely soluble in water but with a strongly alkaline reaction, and the trans-compound $[Pt(NH_3)_2(OH)_4]$ which can be obtained from the corresponding nitrato-compound by treatment with ammonia—it forms yellow insoluble crystals. Palladium gives analogous compounds, e.g. $[Pd(NH_3)_4](OH)_2$. An ammine of osmium hydroxide, $Os(OH)_4 . 2NH_3$, decomposes with some vigour when heated; it is a dark-brown powder, and is formed when a solution of OsO_4 is treated with ammonia. It dissolves with difficulty in acids to a reddish solution, from which it is precipitated unaltered by alkalis, thus acting like a base.

Osmiamic acid, according to Werner and Dinklage,[1] is an imide of osmium tetroxide $\left[Os \begin{matrix} O_3 \\ N \end{matrix} \right] H$, the comparative formulae being :—

Tetroxide : $Os \begin{matrix} O_3 \\ O \end{matrix}$ Osmiamic acid : $Os \begin{matrix} O_3 \\ NH \end{matrix}$.
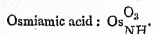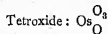
The crystal structure of the ion $[OsO_3N]'$ was shown by Jaeger and Zanstra[2] to be

[1] Ber., 1901, 34, 2698.

[2] Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 610, 787.

nearly tetrahedral, the O and N atoms, as far as X-ray results are concerned, being practically equivalent. This indicates the formula

$$\begin{array}{c} O \nwarrow \quad \nearrow O \\ Os \\ O \swarrow \quad \searrow N \end{array}$$
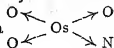
for the ion, the

negative charge being located at the N atom, and OsO_4 is

$$\begin{array}{c} O \nwarrow \quad \nearrow O \\ Os \\ O \swarrow \quad \searrow O \end{array}$$. The
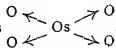
potassium salt is obtained by treating the solution of the tetroxide in KOH with ammonia: $OsO_4 + KOH + NH_3 \longrightarrow [OsO_3N]K + 2H_2O$. This salt forms yellow octahedra and loses its nitrogen on heating to 440° with formation of the blue $[OsO_3]K$.

With concentrated hydrochloric acid, chlorine is evolved and gives the red $\left[Os \begin{array}{c} N \\ Cl_5 \end{array} \right] K_2$.

Salts of the heavier alkali metals corresponding to this substance have also been obtained.

METALLIC OXIDES—ACIDIC

General methods of preparation—Stability—Manganates and permanganates—
Ferrates, chromates, dichromates and polychromates—Halogen derivatives of
chromic acid—Rhenium and masurium

WHEN a metal has several oxides the basic properties of the hydroxides
become less pronounced as the valency of the metal increases. When
a certain limit in valency is reached the basic properties disappear
almost completely and salt formation does not take place to an
appreciable extent. The salts of $Mn(OH)_4$, for example, hardly
exist at all; and when oxides containing more oxygen than the
neutral oxide are formed they have definitely acidic properties. The
oxides of sexa- and septavalent manganese give salts in which they
function only as acid oxides. Another way of stating the result is to
say that as the ionisation into OH ions becomes weaker, that into H
ions increases, and the oxides become more electronegative as the
proportion of oxygen increases. The higher oxides and chlorides of
the metals are more volatile than the lower ones, as they tend to
approach oxygen or chlorine in their behaviour.

Thus acidic oxides are formed only by those metals which can
exert a high valency and thus combine with several oxygen atoms.
The acidic tendency is sometimes shown even in the quadrivalent
condition (Pb, Sn), but appears almost invariably in the quinquevalent and
higher states of the metal. Hence metals in the right-hand half of the
periodic table give acidic oxides. The acids cannot always be isolated
in the pure form, as they are frequently converted into the anhydride
(chromic acid) or suffer extensive decomposition (ferric acid, manganic
acid) or are polymerised (molybdic acid) when liberated from their salts.

The most important of these acids are: manganic, permanganic
and ferric acids; chromic, molybdic, tungstic and uranic acids; vanadic,
niobic and tantalic acids. (The acids of the metalloids arsenic and
antimony and of bismuth are discussed on pp. 731-734; those of the
noble metals on p. 466.)

These acids show great variety in their properties; some are known
only as salts and do not exist even in solution (H_2MnO_4, H_2FeO_4);
others are known in concentrated solution, but decompose when an
attempt is made to isolate them ($HMnO_4$, H_2CrO_4); others, again,

exist in fairly concentrated pseudo-solution, but once isolated are only brought into solution again with great difficulty (molybdic, tungstic, uranic, vanadic, niobic and tantalic acids)—there is no reversible equilibrium in their solutions between the dissolved and the solid material. A similar set of differences exists in the salts of the acids; the acids of iron and manganese form only normal salts, chromic acid also forms salts in which a few molecules of the anhydride are combined with the normal salt (anhydro-salts); while in the other acids of this class the effects of condensation and polymerisation are much more pronounced, and auto-complexes of high molecular weight and great stability are formed. This property is connected with that of forming heteropolyacids (cf. p. 500). It is obvious that comparisons between one group of these acids and another can seldom be drawn with advantage.

Formation and Stability.—The most important method of preparation is common to all these acids: the salts are obtained when a lower oxide of the metal is heated with alkali in the presence of an oxidising agent. When the acidic oxide is the most stable of the oxides of the metal it is formed when the metal itself or its lower oxides, hydroxides or sulphides are roasted in the air, even when alkali is not present (MoO_3, WO_3, UO_3, V_2O_5, Nb_2O_5, Ta_2O_5). The oxides of Cr, Fe and Mn which are obtained in this way are not, however, the acidic oxides but lower oxides (Cr_2O_3, Fe_2O_3, Mn_3O_4), and the higher oxides are formed only when alkali is present. The lower oxides can be fused with caustic potash or soda (or the carbonates) with admission of air, and the oxy-salts are formed, e.g. $Cr_2O_3 + 2Na_2CO_3 + 3O \longrightarrow 2Na_2CrO_4 + 2CO_2$, probably with the alkali peroxide as an intermediate product. The oxidation is more rapidly and easily carried out if alkali nitrates or chlorates are used as oxidising agents, as they provide a more readily available supply of oxygen. It is remarkable that the oxidation of manganese to the manganate stage, K_2MnO_4, is incomplete; when a large excess of alkali is present a melt is obtained which contains only 2·6 atoms of oxygen per atom of manganese instead of the three atoms required by MnO_3. The mass has an intense dark green colour, and Sackur has shown[1] that it contains manganites, i.e. salts of the anhydride MnO_2, mixed with the manganate. The potassium compound has the formula $8K_2O$, Mn_5O_{13}, while that obtained from sodium salts is $4Na_2O$, Mn_2O_5; but it is more likely that solid solutions are formed, and not definite compounds, as there is no indication of an equilibrium between manganite and manganate— the same product is also obtained when potassium permanganate is heated alone or with alkalis. Baryta or lime can be used in place of caustic potash or soda. The formation of permanganate is interesting, for it is not a primary product of the oxidation of the lower oxides, but

[1] Ber., 1910, **43**, 381, 448 ; 1911, **44**, 777.

results from the decomposition and further oxidation of the manganate formed. When MnO_2 is heated with alkali alone, manganate is produced at 130° by the decomposition $3MnO_2 \longrightarrow MnO_3 + Mn_2O_3$, the MnO_3 combining with the alkali. The Mn_2O_3 is oxidised to MnO_2 only at a red heat, when the above decomposition is repeated.

The manganate itself is also decomposed on further heating, with formation of lower oxidation products, and gives a definite dissociation pressure, which for K_2MnO_4 is as follows :

Temperature	.	.	507°	572°	629°	667°
Pressure of oxygen	.	.	11	52·6	221	532 mm.

In a mixture of oxides of manganese and base, such as is obtained when permanganate is heated, the following apparently reversible dissociation pressures are obtained :

Temperature	.	.	505°	560°	600°
Pressure of oxygen	.	.	50	129	400 mm.

Similar conditions obtain in the red melts formed by the fusion of iron compounds with alkali with access of air or addition of nitrate or chlorate. These contain ferrates, e.g. K_2FeO_4, but if formed at too high a temperature the ferrates, like the vanadates, are decomposed. When alkali vanadates are heated oxygen is given off with decrepitation, and if the residue is rapidly cooled a dark mass is obtained which contains vanadium in both the quadrivalent and quinquevalent states. On slow cooling, oxygen is absorbed and a clear red vanadate is obtained.

The normal chromates lose oxygen only at a high temperature, but the polychromates are more easily decomposed ; thus, fused $Na_2Cr_2O_7$ gives off oxygen at 400°. Even CrO_3 is decomposed at high temperatures (p. 477). The salts of the other acids of this group (molybdic, tungstic, niobic and tantalic acids) can be fused without decomposition, or at least without loss of oxygen.

The above discussion indicates the best procedure in the preparation of these salts by the method of fusion with alkalis. When the anhydride of the acid is the commonest oxide of the metal (as with Mo, W, U, Nb, Ta, V) no oxidising agent need be added to the alkali. Niobates and tantalates are made in this way from the naturally occurring iron (manganese) niobate and tantalate (niobite, tantalite), and molybdates can similarly be made from lead molybdate (wulfenite), or from molybdenite MoS_2 after roasting to MoO_3. Vanadates are also prepared from the natural heavy metal vanadates, and tungstates from wolfram (Fe, Mn)WO_4 by roasting it in a furnace to render the iron insoluble and then fusing with sodium carbonate and leaching out the soluble sodium tungstate produced. In the manufacture of sodium uranate from pitchblende, as that salt is insoluble in water, it is converted into soluble sodium uranyl carbonate by addition of sodium bicarbonate, and then precipitated as sodium uranate by addition of sulphuric acid. Oxidising alkali fusions are necessary for the production of the salts of chromium, iron and manganese, since only the lower oxides of these metals are found in nature. Pyrolusite is used as the

raw material for the manufacture of manganates, and chrome ironstone, ferrous chromite, $Fe(CrO_2)_2$, for chromates.

Only in a few instances can the acids be obtained directly by treatment of the ores with acids ; but tungstic acid is formed when scheelite, $CaWO_4$, is treated with sulphuric acid, and niobic and tantalic acids can be prepared by fusing the minerals with potassium bisulphate. The acids remain as an insoluble residue contaminated with other substances, especially TiO_2, from which they can only be separated by conversion into the fluoro-salts (p. 356) and recrystallisation, or separation may be effected by the use of tannin.[1]

The method of oxidation in solution is sometimes employed for the preparation of these salts, but only for those made from lower oxides of the metal—iron, chromium and manganese. The reaction occurs more readily in alkaline solution, and ferric acid is not produced at all in acid solution, as the free acid is unstable. Manganous and chromic compounds are oxidised by lead dioxide, sodium bismuthate or potassium periodate in nitric acid solution, a reaction which serves to detect minute quantities of manganese by the violet colour of the permanganic acid formed. Only chromium is oxidised by hydrogen peroxide and persulphates in acid solution, for permanganates are decomposed by excess of H_2O_2. In sulphuric acid solution the manganese is oxidised to the quadrivalent stage. Chromic salts are oxidised to chromates by permanganates.

In alkaline solution a great variety of oxidising agents can be used : hydrogen peroxide, persulphates, oxides of noble metals, hypochlorites, hypobromites, and other substances convert chromium salts into chromates, and similarly, but less easily, oxidise iron and manganese salts. Electrolytic oxidation is also frequently applied in alkaline solution for all three metals ; an alkaline solution of the metallic salt or a suspension of the hydroxide in alkali is rapidly oxidised at the anode (which should be made of the same metal). Chromic salts are oxidised to chromic acid at the anode even in dilute sulphuric acid solution, and this method is used for the regeneration of the chrome liquors obtained when chromic acid is used on the large scale as an oxidising agent for organic substances. Permanganates and chromates are now usually manufactured by the electrolytic process, and even insoluble chromates like lead chromate (important as the pigment chrome yellow) can be made in this way ; the solution of chromate or of chromic salt is electrolysed with a lead anode, and the lead chromate formed at the anode does not adhere if a little chlorate is added to the liquid. If no chlorate is added the anode becomes coated with the insoluble chromate and the action stops, but the liberation of some chlorate ions prevents the formation of a continuous layer of chromate and thus exposes part of the anode to attack by the CrO_4'' ions.

[1] See Schoeller, *The Analytical Chemistry of Tantalum and Niobium*, London, 1937.

The Manganates and Permanganates.—Manganic acid is probably a weak acid, while permanganic acid is a strong acid. *Manganic acid,* H_2MnO_4, is known only in the form of its salts and cannot be obtained in the pure state or even in aqueous solution; the anhydride MnO_3 is equally unstable. *Permanganic acid,* $HMnO_4$, although unknown in the pure state, can be obtained in aqueous solution or as the anhydride Mn_2O_7. When an attempt is made to isolate manganic acid from solutions of its salts the acid decomposes into higher and lower oxidation products, thus:

$$\overset{VI}{O_2MnO} + 2\overset{VI}{MnO_3} \longrightarrow \overset{IV}{MnO_2} + \overset{VII}{Mn_2O_7}.$$
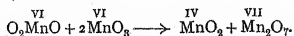
Hence a precipitate of manganese dioxide separates out and the liquid becomes violet in colour owing to the permanganic acid formed. The latter can be reconverted into the green manganate by the addition of alkali, and on acidifying, the violet permanganate and the black precipitate are again produced. Even carbon dioxide suffices to set free the manganic acid from the manganate, and the CO_2 normally present in the air is used technically to cause the transformation by blowing air through the solution from the green melt of manganate. Other acids, both strong and weak, act in the same way provided the acid has no reducing properties, *e.g.* hydrochloric acid cannot be used. The solution of permanganic acid obtained by oxidising manganous salts with KIO_4 in a solution 10 per cent. with respect to HNO_3 is stable for several weeks, in presence of a small excess of KIO_4.

A solution of permanganic acid free from salts can be obtained by decomposing barium permanganate with the calculated quantity of sulphuric acid. It can be concentrated to contain 20 per cent. $HMnO_4$, but beyond that stage begins to give off oxygen. The concentrated solution decomposes readily into the *anhydride* Mn_2O_7 and water, and as the oxide is somewhat volatile it can be recovered from the solution; it is most easily made by dissolving potassium permanganate in fairly concentrated sulphuric acid and warming to 60°. When the salt is added to the cooled concentrated acid, the oxide separates in oily drops—some dissolves in the acid to a green solution, and the rest forms a metallic-looking liquid below the acid. It is explosive, but not excessively so; it can be distilled on warming, giving a violet vapour, and sometimes detonates violently at a moderate temperature or when it comes into contact with oxidisable substances. Organic compounds are inflamed by it, and a black smoke of MnO_2 is produced; in moist air the Mn_2O_7 is slowly decomposed, the resulting oxygen being largely ozonised. The solution of Mn_2O_7 in concentrated sulphuric acid is green, but on dissolving it in water the violet colour of permanganic acid is at once evident.

The solid manganates are not green like their aqueous solutions and melts; the potassium salt, K_2MnO_4, is pale brown to copper colour,

while the sodium salt is black. The permanganates have a metallic lustre which can also be observed in the anhydride Mn_2O_7; in fact, this bronze lustre seems to be peculiar to the higher manganese compounds, though some dyes, like rosaniline, show the same effect. In solution, the brown colour is lost and only the well-known violet persists.

Sodium and potassium manganates are very soluble, but the latter is less soluble when quantities of potassium hydroxide are present. The solubilities are fairly independent of temperature, and the salt must be crystallised from dilute potassium hydroxide. So far no manganates other than those of sodium and potassium have been obtained in the pure state. Of the permanganates, the potassium salt is the best known, as it can be obtained in stable crystals, whereas the sodium salt is deliquescent. The former is not very soluble in cold water; 100 g. of water dissolves:

Temperature	$-0.58°$	$+4°$	$10°$	$20°$	$40°$	$60°$	$75°$
$KMnO_4$		3.0	3.4	4.4	6.5	12.5	22.0	32.4 g.

The solubility diminishes as the atomic volume of the alkali metal increases; thus at $60°$ the solubility of $RbMnO_4$ is only 4.68 g., and that of $CsMnO_4$ 1.25 g. This relation has been noted in the perchlorates (p. 381), which the permanganates resemble in other ways; thus the salts of the alkaline earth metals and of the heavy metals of both classes are very soluble, and are also isomorphous, giving mixed crystals. On the other hand, $NaMnO_4$ does not give mixed crystals with $KMnO_4$, nor does $AgMnO_4$. The manganates are likewise isomorphous with the chromates, sulphates and selenates of the same metals; K_2MnO_4 is miscible with K_2SO_4, as also Na_2MnO_4. $10H_2O$ with the analogous Glauber's salt Na_2SO_4. $10H_2O$. The water of crystallisation in the two series is also the same—the potassium salts are anhydrous, while the sodium salts crystallise with 4, 6 and 10 mols, of water. The permanganates of the alkalis (except Li), of silver, univalent thallium and of barium are anhydrous; the other salts have water of crystallisation: Sr 4 mols., Ca 5 mols., Mg, Zn, Ni, 6 mols. Cd 7 mols., Cu 8 mols. The solutions of the permanganates of the heavy metals decompose on prolonged boiling, and the ill-defined permanganates of aluminium, iron, etc., cannot be boiled at all without decomposition.

The permanganates are powerful oxidising agents in the solid state, and when alcohol is dropped on to solid calcium permanganate it is inflamed. The oxidising property persists in solution, especially when the permanganic acid is set free, as may be seen from the list on p. 164. Almost all substances with reducing tendencies show them in presence of permanganate, which is reduced to the bivalent stage in acid solution and to the quadrivalent stage in alkaline or neutral solution, as in

the latter alkali is set free. With small quantities of such reducing agents as sulphites or alcohol, the reduction only proceeds as far as the manganate stage. Hydrogen sulphide, ferrous and stannous salts, halogen hydracids, H_2O_2 and many other substances can reduce permanganate. Hydrogen reduces the salt at once when in the nascent condition, but only very slowly when in the molecular form. Oxalic acid is only reduced rapidly in the cold when a trace of a manganous salt is present; with the permanganate this gives MnO_2, which serves to reduce the oxalic acid, so that the reaction produces its own catalyst (autocatalysis).

Ferrates.—The ferrates are less stable than the manganates. They decompose even in alkaline solution with liberation of oxygen and separation of ferric hydroxide, but the reaction is diminished when the solution is cold and very strongly alkaline. These salts give dark amethyst to cherry red solutions, and the potassium salt, K_2FeO_4, can be obtained as a dark red powder from concentrated solutions containing much potassium hydroxide. The sodium salt is too soluble to be obtained in this way, but the difficultly soluble purple barium ferrate can be prepared by precipitating the solution of the potassium salt with a dilute solution of a barium salt. This compound is the most stable of the ferrates and can be dried at 100° without much decomposition. The ferrates are probably isomorphous with the manganates, chromates and sulphates.

The Chromic Acids.—The chromates correspond with the manganates in composition and method of formation (p. 471). They do not, however, show the same tendency to break up into compounds of higher and lower valency, and the sexavalent chromium is stable in both acid and alkaline solution. Indeed, the anhydride itself, CrO_3, is deposited in deep red needles, on long standing, from a sulphuric acid solution of a chromate. It can be prepared alternatively by the decomposition of barium or lead chromates with the same acid and subsequent evaporation of the clear solution. No hydrates of this oxide in the colloidal state are known, and the slow formation of the crystals is characteristic, pointing to a slow condensation process. Chromic acid, indeed, shows a marked tendency to form poly-acids by elimination of water, as in the following examples:

$$2H_2CrO_4 - H_2O \longrightarrow H_2Cr_2O_7 \text{ (dichromic acid)},$$
$$3H_2CrO_4 - 2H_2O \longrightarrow H_2Cr_3O_{10} \text{ (trichromic acid)},$$
$$4H_2CrO_4 - 3H_2O \longrightarrow H_2Cr_4O_{13} \text{ (tetrachromic acid)}.$$
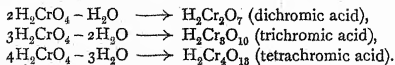
The trioxide probably has a still more highly polymerised molecule with a formula $(CrO_3)_{>4}$. The change from H_2CrO_4 to $H_2Cr_2O_7$ is instantaneous, but the further polymerisations take a measurable time, at any rate when crystallisation ensues. The depolymerisation of CrO_3 on solution in water is, however, very rapid.

The colour of chromium trioxide also indicates that it is highly polymerised, for it is redder than the di- or tri-chromates and is only approached in colour by the tetrachromates. The streak of CrO_3 is darker than that of the tetrachromates. It appears to be depolymerised on heating, for it is partly volatile as a red vapour at 200°, and thus resembles other oxides rich in oxygen (e.g. OsO_4, Mn_2O_7). A good deal decomposes before the temperature of volatilisation is reached, with formation of chromic chromate (p. 482) which is black, and final decomposition to green Cr_2O_3. Chromic anhydride is naturally a powerful oxidising agent and oxidises potassium, sodium, sulphur and phosphorus with the greatest ease. Hydrogen itself, ammonia, and hydrogen sulphide are oxidised when in the gaseous state; organic materials (e.g. alcohol) are inflamed, and even paper is set on fire if some of the compound is left on it. The oxide is very hygroscopic and readily soluble in water: 100 g. water dissolve 164 g. CrO_3 at 0° and 207 g. at 100°.

When dilute solutions of chromates are acidified, the acid is not precipitated like molybdic, tungstic and vanadic acids. On evaporating the solution no acid salts are obtained, but only the polychromates formed from the acid salts by loss of water: $2KHCrO_4 \longrightarrow K_2Cr_2O_7 + H_2O$. This reaction takes place spontaneously, and it may be supposed that there are many $HCrO_4'$ ions in the solution, for it becomes redder on acidifying, indicating the formation of ions of a different structure. Both the chromate ion CrO_4'' and the solid chromates of formula M_2CrO_4 are yellow, but on acidifying, the solutions pass through orange to red. The red colour of the dichromates of formula $M_2Cr_2O_7$ is quite familiar, and the higher chromates are redder still in the solid state. It is thus likely that the various chromate ions, CrO_4'', Cr_2O_7'', Cr_3O_{10}'' and Cr_4O_{13}'', exist together in equilibrium in solution. There is not much evidence for the existence of the tri- and tetra-chromate ions in dilute solution; for addition of water probably occurs, $H_2Cr_2O_7 + H_2O \longrightarrow 2H_2CrO_4$, resulting in the ionic change $Cr_2O_7'' \longrightarrow 2HCrO_4'$, and this change is more marked in the tri- and tetra-chromates, which give dichromates on addition of water. These processes are instantaneous, as can be observed from the absorption spectrum, which does not follow Beer's law—a well-known generalisation which states that the absorption spectrum of a substance is independent of the dilution, and that the same quantity gives the same total absorption in dilute or concentrated solution. Hence, when the absorption alters on dilution of a solution, it follows that a change in constitution has taken place: the mere increase in ionisation does not cause the alteration in the spectrum (cf. Hantzsch, p. 361). In the chromates the deviation from Beer's law is most simply explained as due to a greater complexity in concentrated solutions. Further, the conductivity of chromic acid increases with dilution to $N/125$, but after

that diminishes; while that of potassium dichromate is also abnormal, for it first increases with dilution very slowly, and then much more rapidly after a certain dilution is attained. The first slow increase is explained by the hydration $Cr_2O_7'' + H_2O \longrightarrow 2HCrO_4'$, as the $HCrO_4'$ ions are not very mobile. On further dilution the slow-moving $HCrO_4'$ ions are converted into the CrO_4'' ions, which move more rapidly. Both H_2CrO_4 and $H_2Cr_2O_7$ are strong acids, but they ionise readily only to the monobasic stage, giving one H ion and $HCrO_4'$ and HCr_2O_7'. Dichromic acid is somewhat stronger than monochromic acid. The dissociation of the second hydrogen atom—as often happens with strong polybasic acid—occurs only at great dilution, and here more readily in dichromic acid. In strong dibasic acids, one of the hydrogen atoms ionises almost completely before the dissociation of the second begins. The greater the amount of space between the positions occupied by the two charges the smaller the opposing force; and since in the molecule $HO . CrO_2 . O . CrO_2 . OH$ the hydrogen atoms are more remote from each other than in the molecule $HO . CrO_2 . OH$, the entrance of a second charge in the former is attended with less difficulty.

The relative quantities of chromate and dichromate ions in solution have been determined in many ways. As the conversion of the dichromate to the monochromate ion involves an increase in the number of dissolved molecules, the osmotic pressure, freezing point and boiling point methods are suitable for ascertaining the extent of this hydrolysis. Thus from the equation $H_2Cr_2O_7 + H_2O \rightleftharpoons 2H_2CrO_4$ a constant $K = \dfrac{[Cr_2O_7'']}{[HCrO_4']^2}$ is found. There are many other methods, e.g. that of Sherrill.[1] In solutions of both chromates and dichromates, however, equilibria are set up under the influence of the water which tend to produce normal hydrolysis. The alkali chromates react alkaline, for the CrO_4'' ions which are present have a strong tendency to become $HCrO_4'$ ions, according to the equation $CrO_4'' + H_2O \rightleftharpoons HCrO_4' + OH'$, thus liberating OH' ions. Temperature has not much effect upon these equilibria.

Salts of Chromic Acid.—Most of the normal chromates, M_2CrO_4, are soluble in water or dilute acids. The yellow chromates of barium, lead and univalent thallium, and the dark red salts of silver, of uni- and bivalent mercury and of bismuth are only slightly soluble. The chromates and dichromates of a series of cobaltammines and chromium-ammines are also soluble with difficulty, e.g. $[Co(NH_3)_5NO_2]CrO_4$, $[Co(NH_3)_5NO_2]Cr_2O_7$, $[Co(NH_3)_5Cl]CrO_4$, $[Co(NH_3)_5Cl]Cr_2O_7$, and many others. The chromates of these metal ammines may be precipitated and recrystallised from dilute acid solution, whereas di- or even higher chromates of the heavy metals are obtainable only from very

concentrated solutions. Hence solutions of dichromates, which always contain some CrO_4'' ions, give precipitates of the normal chromates with dilute barium, silver and similar salts. Dichromates of these metals do indeed exist, but can only be produced from acid solutions, which contain scarcely any CrO_4'' ions. $Ag_2Cr_2O_7$, for example, is produced from Ag_2CrO_4 by the action of nitric acid of, at least, 0·075 N strength, and is converted back to the monochromate by dilution. Very dilute acid is required to produce $BaCrO_4$ by this method. Strontium chromate, which can be partially precipitated very readily even from neutral solution, at once dissolves in weak acids like acetic acid. On the other hand, the lead salt is hardly soluble in the most concentrated acids, so that the particular chromate obtained by precipitation depends only on the quantities used. The crystalline polychromates (recognisable by their red colour) may be converted into the yellow monochromates by simple treatment with more water. Polychromates of thallium are also easily prepared. The acid salts proper, having the formula $MHCrO_4$, are unstable and at once give dichromates, two molecules losing one molecule of water.

The different colours of the various monochromates are striking; whereas the majority are coloured yellow, irrespective of solubility, a few of the insoluble ones, such as the silver, mercury and bismuth salts, have an intense purple colour. This points to a difference of structure, for these metallic ions are themselves colourless. There are thus two types: the yellow or normal salts and the purple or pseudo-salts. The red chromates are used as indicators. For example, silver chloride (or cyanide) is less soluble than the chromate, so that it is possible in titrating a soluble chloride with silver nitrate to determine when all the Cl' ions have been removed from solution, for any further addition of silver at once produces the brownish-red tint of the chromate. The coloration vanishes on adding a drop of chloride solution, as the insoluble red chromate is thereby converted into the soluble, pale alkali chromate: $Ag_2CrO_4 + 2NaCl \longrightarrow 2AgCl + Na_2CrO_4$. The well-characterised basic salts of chromic acid are also yellow, the best known of them being the easily soluble sodium salt, $Na_4CrO_5 \cdot 10H_2O$, of a sulphur-yellow colour, and the slightly soluble, bright yellow, bulky calcium salt, $Ca_2CrO_5 \cdot 3H_2O$. The colours of the basic lead chromates are also interesting. If precipitated yellow lead chromate is treated with caustic soda a scarlet mass is obtained, having one of the following formulae: $2PbO \cdot CrO_3$, $3PbO \cdot CrO_3$ or $4PbO \cdot CrO_3$. The colour of chromates, despite its lightness, is very intense, so that mere traces of chromates are able to impart their colour to a solution. The same applies to the dark orange tint of the dichromates. The red colour produced by addition of diphenylcarbazide, $(C_6H_5NH \cdot NH)_2CO$, to acidified solutions of chromates or dichromates is extremely intense.

Of the alkali chromates, those of potassium, rubidium and caesium are notable for the ease with which they crystallise. The normal salts of these metals dissolve more readily than the acid salts, the reverse being true of the sodium salts. The sodium chromate crystals also contain water, the others yield anhydrous crystals. The caesium salts are the least soluble. The following figures give the solubility per 100 g. water:

Temperature .	.	.	0°	30°	60°	105·8°	
K_2CrO_4	.	.	57·1	65·1	74·6	88	g.
$K_2Cr_2O_7$	.	.	4·6	18·1	46·1	109	,,
Rb_2CrO_4	.	.	38·3	44·1	48·8	...	,,
$Rb_2Cr_2O_7$	,	.	...	10·56	...	...	,,

At 30°, 40·5 g. of $(NH_4)_2CrO_4$, and 47·2 g. of $(NH_4)_2Cr_2O_7$, dissolve in 100 g. of water. All the foregoing salts are anhydrous. In contrast to these, the alkaline earth salts and the related lithium compounds contain water of crystallisation (the latter gives a monochromate with 0 and 2 mols. water, the dichromate with 2). The sodium compounds, of which the following are known, are also hydrated: the chromate with 0, 4, 6 and 10 mols. H_2O, the dichromate with 0 and 2; the tri- with 1 and the tetrachromate with 4 mols. of water. The transition temperature of $Na_2CrO_4 . 10H_2O$ $19·525°$, is so sharply defined that the solidifying of the melted salt in its own water of crystallisation may serve as a fixed point in thermometry. By fusion of the decahydrate, an unstable hexahydrate is produced, and can be detected up to 25·9°, this passing into a stable tetrahydrate which loses the rest of its water at 62·8°. The following points on the solubility curve have been chosen to illustrate these changes:

Temperature.	.	.	.	.	0°	19·52°	25·9°	62·8°	80°	100°
G. anhyd. Na_2CrO_4 in 100 g. water					31·7	79·2	86·1	123·3	124·3	126·0

The solubility gradient of the anhydrous salt (i.e. above 62·8°) is thus very slight. The dihydrate of $Na_2Cr_2O_7$ becomes anhydrous at 83°; its solubility is as follows:

Temperature	.	.	.	0°	52°	83°	93°
G. $Na_2Cr_2O_7$	.	.	.	163·0	253·2	417	433

The tetrachromate $Na_2Cr_4O_{13}$ has a solubility of 269·9 g. at 0°.

In the alkaline earth chromates the power of combination with water and the solubility both increase in passing from barium to magnesium. While the barium salt is anhydrous and only slightly soluble (2·04 mg. in a litre of water at 0·88°, and 4·36 mg. at 28·08°), the magnesium salt is very soluble, and hydrates containing 5 and 7 mols. water are known. The solubility of calcium chromate is interesting: there are the anhydrous salt and hydrates containing $\frac{1}{2}$ and 1 mol. H_2O respectively, as well as two different ones with 2 mols. H_2O, and all these five calcium chromates have separate solubility curves. From the curves it is clear that the solubilities of all these chromates *decrease* with increase of temperature, with the exception of one of the dihydrates, of which more dissolves at higher temperatures. These relations are to some extent similar to those in the cerium sulphates (p. 433), and in general (*cf.* pp. 422, 579) calcium compounds are distinguished by their decrease in solubility

with rising temperature. The appended table shows the percentage of anhydrous calcium chromate (using each hydrate) in saturated solution :

Mol. H_2O	0	$\frac{1}{2}$	1	2 (β)	2 (α)
At 0°	4·3	6·8	11·5	10·0	14·75
At 100°	0·42	0·8	3·1	(40°) : 10·4	(45°) : 12·53

Calcium forms acid salts up to tetrachromates ; for basic salts see p. 479.

The solubility of strontium chromate in 100 g. water is at 25°, 0·096 g. ; at 50°, 0·090 g. ; at 75°, 0·080 g.

The polychromates often form various modifications in the solid anhydrous state. Potassium dichromate is known to have this property and occurs in the form of thick, triclinic crystals, which melt at 396° ; large crystals separate from the fused mass on cooling, which are not identical with the original ones. They break up on cooling, as they are unstable at a lower temperature, the purplish colour giving place to the orange red of the dichromate. This decomposition is reversible, the transition temperature being 236°. The rubidium compound, $Rb_2Cr_2O_7$, behaves very similarly and has three modifications. The ammonium compound gives no such change because, as described on p. 446, this salt evolves nitrogen when heated, leaving behind Cr_2O_3. The normal ammonium chromate $(NH_4)_2CrO_4$ is not produced at high temperatures, and even at room temperature ammonia is lost, giving the red dichromate. On the other hand, various stable double salts of ammonium chromate are known, e.g. KNH_4CrO_4, and, like sulphuric acid, chromic acid has a tendency to form these alkali double salts, which are often very complicated. The formula $K_3Na(CrO_4)_2$ serves to indicate the type of compound. The double compounds of the alkali chromates with halides of mercury are of special interest ; their structure is still unknown. The formulae $K_2CrO_4 \cdot 2HgCl_2$, $K_2Cr_2O_7 \cdot HgCl_2$ and $(NH_4)_2Cr_2O_7 \cdot 4HgCl_2$ may be quoted as examples ; and it may also be mentioned that $Hg(CN)_2$ gives similar compounds. These are somewhat similar to the double chlorides of mercury and the cobaltammine bases, e.g. $[Co(NH_3)_6]Cl_3 \cdot HgCl_2$ or $[Co(NH_3)_6]Cl_3 \cdot 3HgCl_2$, etc.

Lead chromate or "chrome yellow" (cf. p. 473) can be precipitated equally well from chromates or dichromates. This compound is isomorphous with lead molybdate, $PbMoO_4$, and is the most insoluble of all the chromates, being also less soluble than most lead salts, except the sulphate. The fact that "chrome yellow" gradually assumes a red colour when exposed to air restricts its use as a paint, although the change can be retarded by mixing a little lead sulphate with it. Here it is not a question of a deepening in colour as a result of an increase in the size of the grains, as is perhaps the cause with HgO (p. 463), because the initial product is distinctly crystalline ; it is rather a definite transition to another form. Indeed, mercury and silver give red precipitates at once. For the behaviour of lead chromate towards alkalis, see p. 479.

It does not seem possible to produce manganese chromate. When a manganese solution is added to a soluble chromate a precipitate is thrown down, but only very slowly, and its properties as a whole point to the manganese being in a higher state of oxidation than the bivalent stage. Consequently the valency of the chromium will be lower than 6, and oxidation and reduction have taken place at the same time. A similar reaction occurs if a chromium salt is mixed with a chromate. It is possible that the substance produced is a chromate of chromium, *e.g.* the resulting brown residue may be accorded a formula $2Cr_2O_3 . CrO_3$; alternatively, compounds of quadri- and quinquevalent chromium may be present. Compounds in which chromium is quinquevalent appear to exist, for if chromium trioxide acts in the cold upon very strong hydrochloric acid, a brown liquid results, from which double compounds of the types $CrOCl_3 . RCl$, $CrOCl_3 . 2RCl$ can be isolated, where R stands for potassium, rubidium, caesium, ammonium, pyridine or quinoline.[1] It is very likely that quinquevalent chromium really exists in these substances, as they form isomorphous mixtures with quinquevalent niobium. Hence the so-called "chromium chromate" probably represents an intermediate stage of oxidation. It is also obtained by heating CrO_3 in dry air, oxygen being evolved; conversely by heating $Cr(OH)_3$ in a stream of oxygen, or by heating chromium nitrate, $Cr(NO_3)_3$, aq. These compounds, of which the brown $2Cr_2O_3 . CrO_3$ and the "chromium dioxide" CrO_2 are the more remarkable, are all insoluble in water; the former is paramagnetic and the latter is black in colour. Other methods of preparing them are, in the wet way by precipitating chromates with a chromium salt, or by reducing the dichromate with nitric oxide, thiosulphate and other agents. The product obtained by these methods is gelatinous.

In the interesting chromium compounds prepared by F. Hein[2] the valency of the chromium has not its usual value—

$$(C_6H_5)_5Cr . OH; (C_6H_5)_4Cr . OH; (C_6H_5)_3Cr . OH.$$
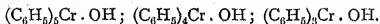
These are all strong bases with a bright orange colour. The compound $(C_6H_5)_4Cr$ is also orange, but is probably polymerised. The higher members of this series of compounds tend to lose phenyl groups easily, and this, together with the common colour, suggests that "phenyl of crystallisation" is present in these compounds. The same applies to the compounds[3] of univalent chromium (?CrCl) formed by the action of phenyl magnesium bromide on $CrCl_3$ or $(C_6H_5)_5CrCl$. If this suggestion is not correct these compounds must have a very abnormal structure.

Oxidation reactions which are brought about by chromates and free chromic acid are fully described elsewhere in this book. The

[1] Meyer and Best, *Z. anorg. Chem.*, 1889, **22**, 192; Weinland and Fiederer, *Ber.*, 1906, **39**, 4042.   [2] Cf. *Ber.*, 1926, **59**, 362.   [3] *Ber.*, 1927, **60**, 749.

oxidation potential is given on p. 164. Although these oxidations often proceed very quickly in acid solution, they go much more slowly in absence of acid. The speed of reaction can sometimes be observed, *e.g.* in the oxidation of hydrogen iodide, arsenious acid and of ferrous salts. Very often a catalytic agent is required to start the action, and ferrous ions, As_2O_3, SO_2, compounds of quadri- and quinque-valent vanadium and others serve this purpose. It is believed, therefore, that the catalyst is at first oxidised to an unstable peroxide, which then in turn oxidises the "acceptor," that is, the sexavalent chromium is first of all reduced to the quinquevalent state, which exerts an oxidising effect, passing through the quadri- to the ter-valent condition, the final product of the reaction.[1]

An obvious difference between chromic and permanganic acids lies in their behaviour towards hydrogen peroxide ; whereas the latter undergoes reduction (p. 408), chromic acid can be oxidised to per-chromic acid (see p. 514). Again, it is possible to obtain a chloride of chromic acid, chromyl chloride, while the manganese acids only suffer reduction by hydrochloric acid.

Chromyl Chloride, Chlorochromic Acid and related compounds.—The hydroxyl groups in chromic acid may be successively replaced by chlorine :

$$[CrO_4]H_2, \qquad [CrO_3Cl]H, \qquad [CrO_2Cl_2].$$

The displacement of one group yields a monobasic acid, chlorochromic acid ; and when both are replaced chromyl chloride is formed. Free chlorochromic acid is not known, but stable salts exist, produced from solutions containing chromic and hydrochloric acids and alkali chloride ; or alkali chromate and hydrochloric acid give the salts on crystallisation :

$$CrO_2(OH)_2 + HCl \rightleftharpoons CrO_2(OH)Cl + H_2O ; \quad CrO_3 + KCl \longrightarrow [CrO_3Cl]K.$$
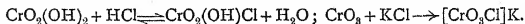
These compounds break down again if recrystallised from pure water, but can be obtained from solutions containing salt or acetic acid. They are well-defined reddish-yellow crystalline substances, and hold much water of crystallisation, in which they melt at a low temperature.

Analogous salts of a hypothetical fluorochromic acid, of a dark red colour, are also known. Bromo- and iodo-derivatives have also been described, but it is doubtful if they really exist, for it is likely that sexavalent chromium would be reduced by hydriodic acid, if not by hydrobromic acid as well.

The employment of larger quantities of HCl, in the presence of strong sulphuric acid (to absorb the water produced), drives the above reaction beyond the chlorochromate stage : $CrO_2(OH)_2 + 2HCl \rightleftharpoons CrO_2Cl_2 + 2H_2O$. To prepare chromyl chloride, a chromate is treated with alkali chloride and strong sulphuric acid ; the CrO_3 and free

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[1] Luther and Rutter, *Z. anorg. Chem.*, 1907, 54, 1.

HCl produced react with one another. Of course, chromyl chloride may also be formed by the direct action of gaseous hydrochloric acid on chromium trioxide: $CrO_5 + 2HCl \longrightarrow CrO_2Cl_2 + H_2O$. Chromyl chloride exists as a dark reddish-brown liquid, which, like its vapour resembles bromine in colour. It has a density of about 2, boils at 117° and freezes at −96·5°. It is soluble without decomposition in carbon tetrachloride, carbon disulphide, nitrobenzene, antimony pentachloride and similar liquids; it is, however, rapidly hydrolysed by water. Thus chromyl chloride must be regarded as the acid chloride of chromic acid. The substance belongs to the same class of compounds as sulphuryl chloride, the acid chloride of sulphuric acid:

$$CrO_2Cl_2 \longrightarrow CrO_2(OH)_2 \qquad SO_2Cl_2 \longrightarrow SO_2(OH)_2.$$
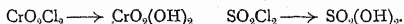
Chromyl bromide and iodide appear to be just as incapable of existence as sulphuryl bromide and iodide. This property is made use of in the detection of chlorine in the presence of the other halogens. If a chloride is warmed with potassium dichromate and sulphuric acid, chromyl chloride distils, and by absorption in alkali produces an alkali chromate. When bromine only is present, however, no such volatile chromium compound is produced. The existence of chromyl fluoride is very probable. A blood-red liquid of large vapour pressure has been obtained from a mixture of chromates, fluorides and strong sulphuric acid.

Rhenium and Masurium[1]

The discovery of these two elements was due to the persistent work of W. Noddack, I. Tacke-Noddack and O. Berg,[2] who utilised the information given by the periodic system as to the properties and

OCCURRENCE OF THE ELEMENTS NEAR NOS. 43 AND 75.

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As
Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
La	Hf	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi
	Th		U			Platinum Ores						

Columbites.

occurrence of the missing elements. Their atomic numbers are 43 and 75 and they are placed under manganese in Group VII—hence

[1] See W. Schröter, *Das Rhenium*, Stuttgart, 1932; I. and W. Noddack, *Das Rhenium*, Leipzig, 1933.

[2] *Naturwiss.*, 1925, **13**, 567; *Z. physikal. Chem.*, 1927, **125**, 264; *Z. Elektrochem.*, 1928, **34**, 627.

being previously called eka- and dwi-manganese—but were not to be found in manganese ores. With a happy inspiration they were sought for in the minerals containing other neighbouring elements. The Periodic Table shows that their neighbours were found in two groups of minerals—the platinum ores on the one hand and the columbites on the other. It is therefore to be expected that these elements might be found in these minerals, and it was in these that they were actually discovered. As their atomic numbers are odd they may be expected to be much less plentiful than their neighbouring even-numbered companions (p. 436), and as the latter are themselves very rare, 43 and 75 might be expected to be rarer still. Actually, the quantities of rhenium in the columbites are of the order of 10^{-7} and there is less in the platinum ores. Masurium is rarer still.

The work of I. and W. Noddack[1] gives the rhenium content of the earth as 10^{-9} g. per g. No single rhenium mineral has so far been discovered; this is due not only to the great rarity of the element but also to its similarity to other elements, which favours dispersion in other minerals. It is most abundant in molybdenum glance, MoS_2, as the quadrivalent ReS_2. All samples of this mineral so far examined contain rhenium, but the highest content is only 10^{-5} g. per g. It occurs as oxide in gadolinite, but the quantity is smaller.

It has only been possible to obtain this very rare element in kilogram quantities at a price of the same order as that of platinum because the method of isolation is relatively simple. This depends on the volatility of Re_2O_7 and the solubility of septavalent rhenium compounds; small amounts of MoO_3 which distil with Re_2O_7 can be precipitated by 8-hydroxyquinoline as $MoO_2(C_9H_6ON)_2$ and Re is then precipitated as nitron perrhenate. In the procedure described by Feit,[2] the ore residues, which contain Mo, Cu, Ni, and Co, derived from materials which contain 10^{-8} g. Re per g. are worked up with such success that in the first year 120 kg. of $KReO_4$ was prepared. The oxidation of the residues gives soluble perrhenates of the heavy metals, which are leached out with water and the slightly soluble potassium perrhenate precipitated (solubility 12 g. per litre). Metallic rhenium can be precipitated by reduction with hydrazine.[3]

The isolation of this element by Noddack, Tacke and Berg was based on the fact that in this part of the system similarities are observed, not merely with elements higher up in the same group, but also with those lying above them to the left (cf. Bohr's classification, p. 25). For instance, titanium shows similarities with niobium and tantalum, and vanadium with molybdenum and tungsten. Consequently rhenium may be expected to have analogies with chromium as well as with

[1] Z. physikal. Chem., 1931, 154, 207.
[2] Z. angew. Chem., 1930, 43, 459.
[3] Kraus and Steinfeld, Z. anorg. Chem., 1930, 198, 386.

manganese. Obviously, its properties will be intermediate between those of tungsten and those of osmium. All these predictions have been verified.

When a few mg. of rhenium had been obtained its individuality was established by the examination of its X-ray spectrum. The same was done for masurium as sulphide, though the separation of this element in weighable quantity is much more difficult. The separation of these elements from the minerals was conducted in such a way as to concentrate the neighbouring elements—Mo, W, Os, and Ru—though when one of these was a main constituent it was separated first. In working up columbite the ore was first subjected to alkali fusion, when the rhenium formed a soluble salt of rhenic acid. The aqueous extract was acidified to precipitate the insoluble acids of Nb, Ta, Zr and Hf. Finally, after a complicated separation, rhenium sulphide was obtained, contaminated with some vanadium. Alternatively, the volatile rhenium oxides may be distilled from the concentrated residues from molybdenum glance.[1]

Very little is known of masurium, but the spectroscopic evidence seems so definite that there does not appear to be cause to doubt its existence. Possibly its chemical properties are so closely allied[2] to those of rhenium that its compounds have not been separated from those of that element (compare Hf and Zr).

Rhenium has now been studied in some detail and its properties are in agreement with its position in the periodic system. The metal, which looks like platinum, is intermediate in properties between tungsten and osmium.[3] It can be obtained by heating perrhenates, oxides or sulphides in hydrogen to 1000°, or by the electrolysis of solutions or fused salts. The metal is soluble in nitric acid, forming perrhenic acid, $HReO_4$. It dissolves but slowly in sulphuric acid and is not attacked by hydrochloric or hydrofluoric acids. Its position in the periodic system indicates that it would be a valuable material for electric lamp filaments but it is at present too scarce for such commercial uses; wires made of rhenium burn in air or in nitrogen one-third as fast as tungsten wires, and are stable in an atmosphere of hydrogen to very high temperatures. Further, pre-heating in a hydrogen atmosphere stabilises rhenium wires against the attack of nitrogen. The general physical properties of the element are to be found in the table on p. 37. It is to be noted that so far an amalgam, a carbide, a nitride or a carbonyl have not been prepared. In its compounds, it exhibits valencies of 3, 4, 5, 6 and 7.

The stability of the septavalent state is one of the chief features of the chemistry of rhenium, though quadrivalent compounds are also known. The colourless perrhenic acid, $HReO_4$, is more stable than either $HMnO_4$

[1] I. and W. Noddack, *Z. anorg. Chem.*, 1929, **183**, 353.
[2] Druce, *Science Progress*, 1933, **27**, 687.
[3] Agte and co-workers, *Z. anorg. Chem.*, 1931, **195**, 129.

or $HClO_4$, though it resembles the latter in the solubility of most of its salts. Thallium and mercurous perrhenates, however, are so insoluble that they can be used for the quantitative determination of the element, and many of the salts differ from permanganates in crystalline form and in amount of water of crystallisation. The solubility increases in the series of cations, Ag—Cs—Rb—K—NH_4, but the salts of all other metals are very soluble. Brucine and veratrine give characteristic precipitates, while the sparingly soluble blue needles formed on addition of methylene blue to a perrhenate serve for microchemical recognition. Mesoperrhenates $M_3^I ReO_5$ are known, e.g. $Ba_3(ReO_5)_2$, formed by treating $Ba(ReO_4)_2$ with excess of baryta; the reaction is reversed by water.

Rhenium differs from manganese in its greater affinity for sulphur, as indicated by the formation of black Re_2S_7, which is so stable that it only begins to lose some of its sulphur at 700° in vacuo. This sulphide is formed when an acidified solution of a perrhenate is treated with H_2S or sodium thiosulphate; in neutral or alkaline solutions the soluble thio-perrhenates $KReO_3S$ and $KReS_4$ are formed. The sulphides ReS_3 and ReS_2 are also black; the element occurs in the latter form in molybdenum glance, and the disulphide is also formed when the heptasulphide is decomposed or by the action of H_2S on quadrivalent rhenium salts.

The following oxides have been described:

ReO_4	Re_2O_7	ReO_3	Re_3O_8	Re_2O_5	ReO_2	ReO_2,H_2O	$Re_2O_3H_2O$
colourless	yellow	red	blue	purplish red	black	black	black

m.pt.   m.pt. 301°

ca. 150°   b.pt. 450°

The first two oxides are formed by heating the metal in oxygen; the droplets of ReO_4 form Re_2O_7 on slight warming. The material described as ReO_4 or Re_3O_8 is probably only a different modification [1] of Re_2O_7. The very stable Re_2O_7 deliquesces in the air to form perrhenic acid, $HReO_4$. This acid is also formed by the decomposition of rhenic acid, H_2ReO_4 on standing. The perrhenates are white, while the rhenates are yellow, the rhenates of the alkaline earth metals being only slightly soluble. The rhenates are formed by evaporating or fusing perrhenates and ReO_2 with excess alkali. They are less stable than manganates, for they pass into perrhenates even in strongly alkaline solution.

Re_2O_7, ReO_3 and ReO_2 are the most definite of these oxides; ReO_3 in early work on the oxides was considered to be Re_2O_5. ReO_3 is obtained by the slow interaction of Re and Re_2O_7 at 250°, or from ReO_2 and Re_2O_7 at 300°; it is isomorphous with WO_3. The oxide Re_3O_8, possibly analogous to molybdenum blue, is formed by the reduction of Re_2O_7 in SO_2 and gives a violet solution in concentrated sulphuric acid. ReO_2 is formed when $NaReO_4$ is heated at 300° or

[1] Hagen and Sieverts, Z. anorg. Chem., 1932, 208, 367.

by heating Re_2O_7 and Re at 650°. Solutions of salts corresponding to this oxide, the rhenites, M_2ReO_3, are made by fusing ReO_2 with caustic alkalis in an inert atmosphere; they are easily oxidised to perrhenates. Hydrated Re_2O_3 is formed from $ReCl_3$ and aqueous caustic soda; it is readily oxidised and liberates hydrogen from water.

ReF_6 (m.pt. 18·5°) is prepared by the direct union of the elements. It is hydrolysed by water and is easily reduced to ReF_4 (m.pt. 124·5°) by hydrogen (200°), carbon monoxide (300°) or sulphur dioxide (400°). $ReOF_4$, ReO_2F_2 and K_2ReF_6 have also been prepared. The highest chloride,[1] which appears to be formed from Re and Cl_2, is $ReCl_5$. It can be sublimed *in vacuo*, and is converted to $ReCl_3$ by heating in nitrogen; the highest bromide is $ReBr_3$. Complex salts, *e.g.* K_2RbCl_6, Rb_2ReCl_6 and various oxyhalide types, are known. Simple iodides have not been prepared, but K_2ReI_6 is obtained by the interaction of $KReO_4$, KI and HI.

[1] Geilmann, Wrigge and Biltz, *Angew. Chem.*, 1933, 46, 223.

METALLIC OXIDES—ACIDIC (*contd.*)

Niobates and tantalates—Uranates and uranyl compounds—Vanadates, tungstates, molybdates—Halogen derivatives of these acids—Hetero- and iso-polyacids: general properties—Complex tungstates and molybdates—Per-acids derived from the higher metallic oxides

THE complexity of the salts of chromic acid is surpassed by that of the salts of molybdic, tungstic, vanadic, niobic and tantalic acids. This property is to some extent related to the weaker nature of these acids, for just as strong acids form very simple salts, weak acids produce more complicated ones, derived from polymerised and partly dehydrated forms. These polymerised acids often occur in the colloidal state, *e.g.* silicic and stannic acids. This property also appears in the acids of the above metals; and although the outward similarity of formula may suggest a resemblance with stronger acids, *e.g.* the isomorphism of lead chromate with lead molybdate, other similarities are scarcely ever present. Molybdic acid is most comparable to chromic acid. The tungstic and vanadic acids show greater differences, while uranic, niobic and tantalic acids are altogether different. The properties of these latter acids will be discussed first, and then the character of the intermediate ones will become plainer.

Niobic and Tantalic Acids.—These very weak acids may be compared with silicic and stannic acids in many of their properties (*cf.* p. 816 *et seq.*). They are precipitated from soluble salts by acids, and niobic acid is formed when the pentachloride, $NbCl_5$, is hydrolysed by water. As with silicic acid, these methods often give a clear liquid at first, which gradually becomes cloudy and a precipitate appears. If the solution of niobium pentachloride is dialysed, the hydrochloric acid can be removed without coagulation; precipitated niobic acid may also be obtained in colloidal solution by digestion with pure water. If the niobic acid is precipitated from concentrated solution in hydrochloric acid, the excess of acid redissolves it, so that it is doubtful whether this solution is colloidal or whether the chloride is produced again. This behaviour is characteristic of the entire group of these acids. Similar solutions may be obtained by fusion of a niobate or tantalate with potassium bisulphate, and extraction of the mass with water—a process used in the analysis of niobium and

tantalum ores; generally the solutions become cloudy and the acids are precipitated. Acid salts of niobic and tantalic acids do not exist, but many different types of salts derived from complex acids can be prepared by fusing the base with $Nb(Ta)_2O_5$, by the action of alkali hydroxide or carbonate on solutions of the very characteristic oxyfluorides of niobium and tantalum, and by many other methods. Among niobates the following have been analysed; the figures show ratios of acid to base:

4:1   3:1   2:1   3:2   4:3   7:6   8:7   1:1   ...
4:5   3:4   2:3   5:16   3:5   1:2   2:5   1:3   1:4

Similar tantalates exist, but conductometric and potentiometric titration affords no evidence of definite potassium tantalates.[1] All these combinations do not correspond to definite niobates, but many of them are compounds and are well crystallised. Ordinary niobates contain the base and acid radicals united in the ratio, base : $Nb_2O_5 = 1 : 1$, corresponding to the nitrates, but "pyro-" and "ortho-" niobates are not chemical entities.[2] The best known is sodium niobate, crystallising with three molecules of water. Some of the alkali niobates are soluble in water, but most are insoluble. Only the tantalates of the type $4M_2O . 3Ta_2O_5$ dissolve in water. Tantalic acid is precipitated from solutions of these alkali salts on adding potassium chloride or ammonium sulphate, a property which is paralleled in certain stannates.

The pentoxides Nb_2O_5 and Ta_2O_5 are obtained as white, amorphous, insoluble powders by heating the hydroxides to redness, or by evaporating the salts with sulphuric acid and extracting the residue with water, as in the preparation of silica. After ignition, like SiO_2 and MoO_3, they are insoluble in acids other than hydrofluoric acid. They are not volatile on heating, and are not reduced, but Nb_2O_5 assumes a yellow colour. Nb_2O_5, however, volatilises completely on heating strongly in hydrochloric acid gas, a reaction which also takes place with V_2O_5, MoO_3 and WO_3 (cf. p. 494). Nb_2O_5 becomes crystalline when strongly ignited; it can also be recrystallised from fused borax.

Unlike vanadic, molybdic and tungstic acids, niobic and tantalic acids do not form many complex compounds with other acids, but oxaloniobates and oxalotantalates are known.

Uranic Acid and Uranyl Compounds.—As the acidic character of related elements decreases with rise of atomic weight, uranium, the heaviest element, might be expected to show no strong acid-forming powers, even when sexavalent. Actually, UO_3 not only acts like an acid anhydride, giving the uranates, but the hydroxide $UO_2(OH)_2$ can also function as a base, and its (OH) groups be replaced by acid radicals. The remainder of the molecule (UO_2) is called "uranyl"

[1] Britton and Robinson, J. Chem. Soc., 1933, 419.
[2] Britton and Robinson, ibid., 1932, 2265.

and plays the part of a metallic radical, forming a chloride, UO_2Cl_2, a nitrate, $UO_2(NO_3)_2$, and many other uranyl compounds. There is no proof that uranyl chloride breaks down into the ions $UO_2\cdot\cdot$ and $2Cl'$; neither conductivity measurements nor its general behaviour on electrolysis give a definite decision on this point, but the above conception of the uranyl compounds corresponds best with the facts.

Uranic acid is not well characterised in the free state. Alleged hydroxides, e.g. H_2UO_4 and $H_2UO_4 \cdot H_2O$, are obtained by warming with water the uranium trioxide produced by heating the nitrate, but probably, as with niobic and tantalic acids, these are only hydrogels. Clear colloidal solutions are obtained if a little uranyl nitrate is added to some of these gelatinous substances. These solutions, like the gels themselves, are yellow. On drying, UO_3 is left as a yellow or brick-red amorphous powder. UO_3 is also obtained when ammonium uranate or uranyl nitrate is cautiously heated in a stream of oxygen to a temperature not exceeding 450°; at higher temperatures some oxygen is lost and U_3O_8, i.e. UO_3, U_2O_5, is formed. Very strong heating causes further evolution of oxygen and gives U_2O_6, i.e. $UO_2 \cdot UO_3$. The dissociation pressure of U_3O_8 is 108 mm. at 850° and 315 mm. at 1165°.

Some of the uranates are derived from the acid H_2UO_4, but more often from the pyro-acid $H_2U_2O_7$; only the sodium and potassium salts of a more complicated set of compounds, containing 1 mol. of base to 6 mols. UO_3, have been isolated (cf. polychromates). All the uranates, including those of the alkalis, are insoluble in water; in this respect they closely resemble the tantalates. The best known is sodium pyro-uranate, or uranium yellow, $Na_2U_2O_7 \cdot 6H_2O$, used in the manufacture of uranium glass, and produced by precipitating a uranyl salt with caustic soda. The ortho-uranates are prepared by fusing a mixture of UO_3 with the requisite quantity of base. Although uranates of the alkaline earth metals are known, the only heavy metal uranate definitely described is silver uranate, which is prepared from silver oxide and uranyl nitrate as an orange-red precipitate. Hydroxylamine uranate $(NH_2OH)_2 \cdot H_2UO_4$ is of interest as it explodes on sudden heating[1]; in thin layers it decomposes completely at 125°, ammonia and water escape, but N_2O and N_2 are left dissolved in the solid residue. These gases are evolved only when the residue is heated to 300° in vacuo, or when it is dissolved in acids. This seems to be a case of a solid solution of gases similar to that of helium in certain minerals and indicates that the gases are not chemically combined.

Unlike the uranates, the uranyl compounds are extremely soluble. They possess a distinctive, brilliant and glittering greenish-yellow colour, and are strongly fluorescent. This fluorescence is still visible in solution, and probably the catalysing powers which the uranyl compounds exhibit in the presence of light are associated with this

[1] Kohlschütter and Vogdt, Ber., 1905, 38, 1419.

property. The reactions brought about are partly oxidising (in conjunction with the oxygen of the atmosphere) and partly hydrolytic, such as the breaking down of the polysaccharoses, saponification of fats and the splitting-off of ammonia from amino-acids, etc. Many of the uranyl salts are decomposed by light,[1] e.g. the oxalate yields uranous oxalate, CO_2, CO and formic acid; hence oxalic acid decomposes in the presence of a little uranyl nitrate. The most useful uranyl compound is the nitrate $UO_2(NO_3)_2.6H_2O$, obtained by dissolving uranic oxide in nitric acid. It forms lemon-yellow, rod-like crystals which are hygroscopic, melting at 59°, and very soluble in water (at 12.3°, 67.4 g. dissolve in 100 g. water). The anhydrous chloride, the sulphate with 3 and the acetate with 2 mols. of water of crystallisation are also made on the large scale. If a solution of potassium dihydrogen phosphate reacts with uranyl acetate in neutral or acetic acid solution, the monohydrogen uranyl phosphate UO_2HPO_4 is precipitated; but when ammonium salts are present the compound $UO_2(NH_4)PO_4$ is produced, the reaction being quantitative in boiling solution. In this way phosphoric acid is determined volumetrically with a uranyl solution, for any excess of uranium may be detected by the brown coloration of potassium ferrocyanide, used as an outside indicator.

The uranyl compounds are characterised by their tendency to build up complex molecules with salts of monobasic acids, such as nitric and acetic acids. The uranyl double nitrates have the formula $M^I[UO_2(NO_3)_3]$, the acetates $M^I[UO_2(CH_3CO_2)_3]$ aq., in which M may stand for many metals. Sometimes several metals may be present in the same molecule, e.g. $NaM^{II}(UO_2)_3(CH_3CO_2)_9.6H_2O$ where M^{II} is Cu, Mg, Zn, Co, Ni, etc.; some of these triple salts are useful in the detection and gravimetric determination of sodium. Double sulphates, too, are known, and the double carbonates are of importance in the purification of uranium compounds. Although uranyl carbonate itself is unstable, there is a whole series of double alkali carbonates, such as $K_4UO_2(CO_3)_3$, $(NH_4)_4UO_2(CO_3)_3$, $(NH_4)_6(UO_2)_2(CO_3)_4.4H_2O$, $(NH_4)_4UO_2(CO_3)_3.2H_2O$, etc., which have been much discussed on account of their optical properties. Their solubility makes it possible to separate uranium from calcium, aluminium and the rare earths, except thorium and zirconium. There are also complex phosphates of uranium. Like niobic and tantalic acids, uranic acid shows but little tendency to form heteropoly-acids, thus differing from the acids of vanadium, molybdenum and tungsten. The replacement of more than one oxygen in UO_3 by a negative group has, up to now, only been observed in the compound UF_6 (p. 357).

For per-uranates see p. 518.

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[1] See, e.g., papers of E. Baur, Ber.; Z. physikal. Chem.; Helv. Chim. Acta, 1918 ff.

Vanadic Acid (for preparation see p. 471).—Vanadic acid has a more pronounced acidic character than the acids just described, and occupies a position intermediate between these and the stronger acids of the metals such as chromic acid. Vanadic acid has a tendency to polymerise, and therefore forms colloidal compounds and complex salts. A very bulky reddish-brown gelatinous precipitate is obtained when a vanadate solution is treated with acid. The gel dissolves both in acids and alkalis. The acid solution cannot be regarded with certainty as a sol for the colour of the solution is somewhat yellow. Vanadium compounds are present with a structure VO_2X or VOX_3, X standing for a univalent acid radical. True colloidal vanadic acid is a blood-red liquid, produced by washing with water the pentoxide obtained by careful heating of ammonium vanadate. The gel previously described gives a similar solution when washed out with water. Very minute (rod-shaped) particles can be seen under the ultramicroscope, as in molybdic acid (*cf.* p. 497). The solution is stable to heat and does not coagulate at the boiling point, but it is very sensitive to electrolytes, *e.g.* sodium and potassium chlorides cause coagulation. Traces of acids produce the same effect, but, as stated, larger quantities bring about complete solution, accompanied by a lighter coloration of the liquid.

Vanadic acid gel dissolves in bases to give salts of various classes, most of which have beautiful colours. When the metal ion itself is not coloured, colourless solutions and salts are produced by using excess of base, which gives ortho-, pyro- and meta-vanadates, *e.g.* K_3VO_4, $K_4V_2O_7$, KVO_3. The meta-form is the most stable; the others are formed only in the presence of a large excess of base. The ortho-vanadates obtained when the base is fused with V_2O_5 are converted into pyro-salts on recrystallisation. All these vanadates in solution show ageing effects.[1] Ammonium vanadate, NH_4VO_3, on account of its slight solubility, especially in presence of ammonium ions, is used in the isolation of vanadic acid from solution. The ortho- and pyro-forms do not exist. These colourless salts are quite different from the coloured "acid" vanadates. Their solutions are frequently orange-red, like the dichromates. There are more important resemblances between the chromates and vanadates; *e.g.* in the solutions of the poly-vanadates the various salts form equilibrium mixtures like those present in the solutions of the polychromates. The white vanadates of the formula MVO_3, when dissolved in water, yield slightly yellow solutions; even with ammonium vanadate the coloration is distinct. Mere solution causes some loss of base, with formation of acid "salts," but these salts have not a true acidic nature and may be compared with the polychromates. They are derivatives of condensed acids which have resulted from the elimination of water from several molecules of the simple acids. The polyvanadates are more numerous than the

[1] Britton and Robinson, *J. Chem. Soc.*, 1930, 1261; 1932, 1955; 1933, 512.

corresponding chromium compounds and resemble the niobates in their complexity. The following potassium salts are known:

$2K_2O, 3V_2O_5, 2H_2O$ $K_2O, 2V_2O_5$ $3K_2O, 5V_2O_5$

$2K_2O, 5V_2O_5, 12H_2O$ $K_2O, 3V_2O_5$ $K_2O, 4V_2O_5, 1\frac{1}{2}H_2O$

$2K_2O, 9V_2O_5$
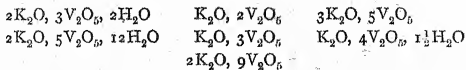
A probable theory, worked out from physico-chemical researches, assumes that the parent compound of such salts is an acid containing six atoms of vanadium, viz. $H_4V_6O_{17}$; three of the hydrogen atoms are easily replaced by metals, the fourth only with difficulty. The theory does not exclude the possibility of other condensed acids. Vanadates, even when possessing the same empirical formula, often have different colours—a fact which is in favour of the hypothesis. While, for example, many alkali polyvanadates are of a beautiful orange-red tint and form transparent crystals, others give golden scaly masses with a metallic lustre. The vanadate $K_2O, 2V_2O_5$, aq. exists in both modifications. The forms with metallic lustre are probably derived from more highly condensed acids. The richer the V_2O_5 content of the alkali salt the smaller is the solubility in water. Since the solutions, like those of the chromates, contain equilibrium mixtures of acids, of which the composition alters with change of temperature, a more acid vanadate often separates on warming. Thus a solution of K_2O, $2V_2O_5$, on being heated, gives crystals of $K_2O, 3V_2O_5$, the mother liquor containing K_2O, V_2O_5.

The vanadates of the alkaline earths and of a few of the heavy metals (Zn, Cd) are soluble in water, but most of the latter are insoluble. The formation of double salts with the alkali vanadates, e.g. the manganese-potassium and nickel-potassium compounds, shows their complexity.

The *pentoxide*, V_2O_5, or vanadic anhydride is produced when ammonium vanadate is heated in air. There must be free access of oxygen, otherwise a vanadium nitride is formed, which cannot be readily converted into the oxide. V_2O_5 is a reddish powder which appears darker in colour when hot, melts at 658°, and boils at an extremely high temperature. The fused oxide, on solidification, forms glittering brownish-red crystals, which sometimes appear black owing to the presence of reduction products, which can be reoxidised by roasting in the air. V_2O_5 is not soluble in water, but gives colloidal solutions. It is soluble in alkalis, even when roasted, but dissolves with difficulty in acids. Its behaviour with hydrochloric acid gas is interesting; when heated in this gas it volatilises, giving a reddish-brown vapour, which can be passed through a glass tube a yard long without condensing. The first action that takes place is: $V_2O_5 + 6HCl \longrightarrow 2VOCl_3 + 3H_2O$; owing to the reaction being reversible the $VOCl_3$ is attacked by the water. If, however, the

gaseous product is dried quickly, this decomposition is reduced to a minimum, and the $VOCl_3$ can be isolated as a solid. V_2O_5, which has been formed in this way, has the properties of an aerosol, and forms a fog difficult to coagulate. It also dissolves in strong hydrochloric acid the solution having a dark brown colour, which rapidly becomes paler when the liquid is diluted.

Vanadic acid, like chromic acid, is a good oxidising agent, although vanadic acid is the less powerful. Oxidations carried out with it are accompanied by very characteristic colour changes. For example, during the oxidation of sulphurous acid to sulphuric acid, the vanadium is reduced to the quadrivalent state with production of a blue colour. Vanadites, e.g. $Na_2V_4O_9$ correspond to this stage of oxidation; the salts $VOX_2(X = F', Cl', Br', H_2PO_2', $ etc.) also contain V^{IV}. Permanganate converts the vanadium back to the quinquevalent condition so sharply that the volumetric determination of vanadium is based on this principle. Phosphorous, hydrobromic and hydriodic acids reduce vanadium pentoxide easily. Vanadium compounds are useful as contact catalysts in oxidation and reduction processes, owing to the ease with which the quadrivalent compounds pass to the quinquevalent state (cf. p. 567). Per-vanadic acid (cf. p. 516) may play a part in these reactions. (For complex acids of vanadium see p. 500 et seq.)

Tungstic Acid.—(For the preparation of tungstates see p. 472.) The free acid is a colloidal substance obtained by the precipitation of soluble tungstates with acids. In hot solution it separates as a yellow, amorphous substance, of empirical formula H_2WO_4; but in the cold a white voluminous substance is formed, which probably contains another molecule of water. Both forms are difficult to filter, and are best washed by decantation. The complete separation of the white modification takes place slowly; when acid is added cautiously it remains in solution, which may then be dialysed, and on evaporation a gelatinous mass is left. This hydrogel is somewhat soluble in water. The yellow form gives a clear solution less easily, but when washed with water readily yields a murky sol, the formation of which is a source of error in the determination of tungsten by precipitation of tungstic acid with subsequent conversion to WO_3. Probably the difference between the white and yellow forms lies in the size and hydration of the particles. It is possible, however, that their molecular structure is not the same, for tungstates have a very varied constitution (cf. p. 510).

The so-called *metatungstic acid*, $H_2W_4O_{13}$, $8H_2O$, is a third modification, and is often present in liquids from which the white colloid has separated. Pure metatungstic acid is obtained by treating a soluble metatungstate with acid (cf. p. 511). Metatungstic acid remains in solution, and is extracted with ether. The liquid separates into three layers: the upper one consists principally of ether, the middle chiefly of water, and the heaviest one contains metatungstic acid usually mixed

with a little water and ether. On concentration, the acid separates out as large, colourless octahedra. Solutions of the acid can also be obtained from the barium salt and sulphuric acid. Metatungstic acid is decomposed in concentrated solution, with formation of the white and yellow varieties, but is very stable in dilute solution, even when boiled. (For salts of tungstic acid see p. 510.)

On ignition of tungstic acid, the *trioxide* WO_3 is formed. This very stable compound can also be made by heating the metal to redness in air, or by roasting the sulphide. The ordinary form is amorphous, but becomes crystalline when strongly heated. It melts at $1300°$-$1400°$. Its lemon-yellow colour changes to orange on heating. WO_3 is insoluble in acids but, like the other oxides derived from these acids, it is very soluble in alkalis. With hydrogen chloride, WO_3 gives a volatile product in the same way as vanadium pentoxide (*cf.* p. 494), but a higher temperature (about 500°) is required.

Tungstic acid, like molybdic, niobic and tantalic acids, is not a strong oxidising agent. It is, however, reduced when heated in a stream of dry hydrogen. An oxide of a blue colour, intermediate in composition between WO_3 and WO_2, is obtained. The interesting "tungsten bronzes," which are made by reduction of alkali or alkaline earth tungstates with hydrogen or molten zinc, are possibly related to this intermediate oxide. Tungsten bronzes[1] appear to possess the composition M_2O, WO_2, xWO_3, where x has a range of 1-7. They are characterised, as their name suggests, by a bronze metallic lustre and are among the best conductors of the electrical current. Their colours vary, and are of a rich, metallic yellow, red, blue, etc. Physical state (*e.g.* dryness, dampness) affects their colour. They crystallise in needles or cubes, and are extraordinarily inert towards reagents; many of them are not affected by hot *aqua regia* or by aqueous alkalis. These properties explain the difficulty of purifying them and also why their structure is unknown. Probably they are mixtures, for even a varying temperature causes remarkable changes in physical structure; for example, the yellow sodium derivative consists of the equilibrium mixture

$$3(Na_2O, WO_2, WO_3) \rightleftharpoons Na_2WO_4 + 2Na_2W_2O_7 + 3W,$$
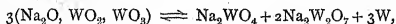
of which the equilibrium constant varies with the temperature.

Molybdic acid has properties closely related to those of the preceding acids. Thus it is precipitated from solutions of its salts by acids, the precipitate dissolving in excess, like niobic acid, vanadic acid, etc. The precipitate is a bulky white one and crystallises in small needles. The resemblance of molybdic acid to a colloidal substance is very great in spite of its crystalline character. Possibly white H_2MoO_4 can be precipitated in two forms, for one kind is

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[1] *Cf.* v. Knorre, *J. prakt. Chem.* [2], 1883, 27, 49.

quite soluble in water (100 g. of water dissolving 0·21 g. at 14·8°, and 0·52 g. at 80°), while others give a colloidal suspension, as do tungstic, vanadic, niobic and tantalic acids. Besides this white form a yellow variety exists, having the formula $MoO_3, 2H_2O$, which separates in light yellow, sparkling crystals when a solution of ammonium molybdate containing excess of nitric acid ("molybdate mixture") is allowed to stand. The process is a very slow one, for the mixture is fairly stable, but it is accelerated by inoculation and by maintaining the original concentration of the solution. As with vanadic acid, the freshly precipitated acid redissolves in excess of mineral acid, *e.g.* nitric acid. The process does not appear to be one of peptisation, and the possibility of a compound "molybdenyl nitrate" $MoO_2(NO_3)_2$, analogous to uranyl nitrate, might be supposed, but there is no proof of its existence. Moreover, the molybdic acid—nitric acid solution exhibits the Tyndall effect. It is also coagulated by gelatine solution, redissolving in excess of the reagent. The colloidal particles are small, and the liquid is able to diffuse through membranes; it also conducts electricity like a true electrolyte, and is a strong acid. Freezing point determinations indicate the existence of complexes containing eight molecules. This suggests the presence of an isopolyacid, which explains its strong acidity, for polymerisation always strengthens electro-chemical properties. Molybdic acid has been termed a "hemi-colloid," as it is doubtful whether it is a true colloid.

The yellow dihydrate dissolves more readily in warm water than the white variety. The solubility per 100 g. water is as follows:

Temperature	.	.	.	23	50	79	100°
G. MoO_3 .	-	.	.	0·18	0·64	1·74	4·29

These figures do not apply when taken in the reverse order, for on cooling, molybdic acid separates very slightly, if at all. It is therefore assumed that a change of structure accompanies the act of solution; probably another polyacid is formed.

Molybdenum Trioxide.—The hydrates of molybdic acid are easily dehydrated, with formation of MoO_3. This oxide does not recombine with water, so that it is not a simple acid anhydride. It is also produced when ammonium molybdate is roasted in air or evaporated with nitric acid, the resulting ammonium nitrate being washed out with water. MoO_3 is a white amorphous powder, which turns yellow when heated. It melts at 791°, and on cooling the fused mass yields bright needle-shaped crystals which retain the yellow colour. The oxide most nearly related to it is vanadium pentoxide, but the latter is not so volatile. MoO_3 sublimes when heated in the Bunsen burner, giving colourless, glittering plates. They are often produced during the gravimetric estimation of molybdenum, which is precipitated as the sulphide, and changed to the oxide MoO_3 by heating in an open crucible; the

temperature must not be allowed to rise too high, or some of the MoO_3 will be lost by volatilisation. MoO_3 which has been strongly heated is insoluble in most acids; it will dissolve in hydrofluoric acid, like many oxides of this group, and also in concentrated sulphuric acid. The presence of certain organic acids, with which molybdic acid forms complex compounds, increases the solubility. It is very soluble in aqueous or fused alkalis. Fused salts with an alkaline reaction, such as borax and soda, serve equally well as solvents.

Molybdic acid is a weak oxidising agent, comparable with vanadic acid. It will oxidise, for example, sulphurous, hydrobromic and hydriodic acids. Its volatility in hydrogen chloride, a property possessed, as already described, by V_2O_5, WO_3, etc., is very marked. At 150° complete volatilisation takes place, and a compound $MoO_3, 2HCl$ sublimes in white needles. This substance is soluble without decomposition in organic media, and probably has the formula $\left[Mo \begin{matrix} (OH)_2 \\ O \\ Cl_2 \end{matrix} \right]$

Its crystalline salts, the chloro-oxymolybdates, have an isomeric structure $\left[Mo \begin{matrix} O_2 \\ Cl_2 \end{matrix} \right] M_2$; they are colourless or slightly yellowish green. The easy volatility of molybdic acid in gaseous hydrochloric acid forms a method of separation from the other acids of this group.

Molybdenum Blue.—The deep blue colloidal liquid obtained by the partial reduction of molybdic acid is a very peculiar substance; evaporation gives a glassy, almost black residue, and when the colloid is coagulated by adding an electrolyte a dark blue powder is formed. The composition of these substances approximates to $MoO_2, 4MoO_3, xH_2O$. The blue solution is not formed in presence of alkali—owing to production of the brown hydroxide $Mo(OH)_5$. Molybdenum blue is also unstable in strongly acid solutions. Hence neutral or weakly acid solutions of molybdates are employed for the preparation. They may be reduced by electrolysis, by hydriodic acid, sulphur dioxide, hydrogen sulphide, zinc and other base metals generally. These latter agents can also convert a suspension of solid molybdic acid into the blue solution. Metallic molybdenum may also be used as a reducing agent, the excess of metal being removed by filtration. The use of organic reducing agents is interesting, for these reactions are so strongly influenced by light that the rate of formation of molybdenum blue serves as a measure of the light intensity. Paper soaked in ammonium molybdate becomes blue on exposure to light, and is used in photography. The colour gradually fades, however, as the molybdenum blue is converted into MoO_3 by the oxygen of the air. A pure colloidal solution of the blue can be obtained from ammonium

molybdate and sulphuretted hydrogen; the liquid may be dialysed and the colloid precipitated with alkali salts. If the coagulation occurs in hot solution the precipitate readily redissolves in water, but when precipitated in the cold it dissolves more slowly but in greater quantity; it is also soluble in some organic solvents. Positive colloids, $Al(OH)_3$, $Fe(OH)_3$, cause coagulation, for molybdenum blue is a negative colloid. It can dye fibres, especially silk, and also inorganic gels, *e.g.* aluminium hydroxide gel. The compound cannot be completely dried, for it decomposes above 100° into MoO_2 and MoO_3, which can recombine at a lower temperature; molybdenum blue is also obtained from a mixture of quinque- and sexa-valent compounds of molybdenum, and also by carefully oxidising compounds of a lower valency, which easily pass into the sexavalent stage.

The chemical constitution of molybdenum blue has not yet been determined. It is unlikely that molybdenum blue is a mere salt, in which molybdenum in the lower state of valency acts as the basic component; the existence of a complex compound between the molybdenum of higher valency and that of lower valency is more probable. The dyeing properties, moveover, might be explained by a tautomeric structure. Molybdenum blue is obviously related to the blue oxide of tungsten (*cf.* p. 496), and even to the tungsten bronzes, although molybdenum blue contains no alkali.[1]

Halogen Derivatives of Molybdic, Tungstic, Vanadic, etc., Acids.—Only the salts of these substituted acids are known. They are analogous to chloro- or fluorochromic acid (p. 483), but contain a larger proportion of halogen. The fluorine derivatives are the most stable, *e.g.* :

$$\left[\mathrm{Mo}^{O_2}_{F_4}\right]K_2 \qquad \left[\mathrm{Mo}^{O_3}_{F_2}\right](NH_4)_2 \qquad \left[\mathrm{Mo}^{O_3}_{F_2}\right]NH_4 \qquad \left[\mathrm{Mo}^{O}_{F_5}\right]K$$

$$\left[\mathrm{W}^{O_3}_{F_3}\right](NH_4)_3 \qquad \left[\mathrm{V}^{O}_{F_5}\right]K_2 \qquad \left[\mathrm{Nb}^{O}_{F_5}\right]K_2 \qquad \left[\mathrm{Ta}F_7\right]K_2 \qquad \left[\mathrm{U}^{O_2}_{F_3}\right]Na, \text{ etc.}$$
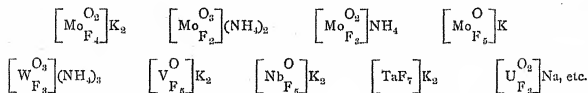
They are produced by dissolving the acid anhydrides and alkali fluorides in aqueous hydrofluoric acid, and may be compared with the fluoro-iodates, *e.g.* $\left[\mathrm{I}^{O_2}_{F_2}\right]K$, fluoro-tellurates $\left[\mathrm{Te}^{O_3}_{F_2}\right]K_2$, fluoro-titanates, fluoro-zirconates, etc. In these compounds the oxygen of the oxysalt is replaced to a variable extent by fluorine. There are similar compounds with the other halogens, *e.g.* :

$$\left[\mathrm{Mo}^{O_2}_{Cl_4}\right]K_2 \qquad \left[\mathrm{Mo}^{O_3}_{Br_3}\right]H_3 \qquad \left[\mathrm{U}^{O_2}_{Br_4}\right]K_2 \qquad \left[\mathrm{W}^{O_3}_{Br_3}\right]K_2, \text{ etc.}$$

There are scarcely any bromine and iodine derivatives of the highest degree of oxidation ; thus the sulphuryl and chromyl chlorides and fluorides are known, but not the iodo- and bromo-compounds. This is partly due to the larger atomic volume of bromine and iodine, and partly because hydrobromic and hydriodic acids

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[1] *E.g.* see Biltz, *Ges. Wiss. Göttingen*, 1904, 5 ; 1905, 141 ; *Ber.*, 1904, 37, 1095.

are strong reducing agents. These compounds can be resolved into molecular components :

$$\left[W{O_3 \atop F_2}\right](NH_4)_2 = WO_3, 3NH_4F \qquad \left[V{O_2 \atop F_2}\right]K_2 = VO_2F, 2KF ;$$
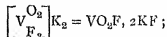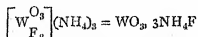
they were formerly considered to be double halogen compounds.

The fluoro-phosphates, -sulphates, -selenates and -dithionates discovered by Weinland and Alpha[1] are made by crystallising phosphates, sulphates, etc., from hydrofluoric acid solution. According to Weinland, they have a constitution different from that of the above compounds, the oxygen attached to the non-metal is not replaced by fluorine, but hydrogen fluoride is combined with the alkali metal. The compounds are therefore comparable with the acid fluorides of the alkali metals and have the formulae

$$[K(HF)]H_2PO_4 \qquad [K_2(HF)_2]S_2O_6 \qquad [(NH_4)_2(HF)_2]SeO_4, \text{ etc.}$$
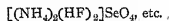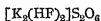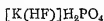
Polyacids

The term "polyacid" is applied to acids which contain several acidic radicals ; *e.g.* the pyroacids $H_2S_2O_7$ or $[O(SO_3)_2]H_2$, $H_4P_2O_7$ or $O(PO_3)_2]H_4$ are true polyacids, but the name was originally used for acids having a large number of radicals, *e.g.* tetrachromic acid, $H_2Cr_4O_{13}$ (p. 476), *i.e.* $[O(CrO_3)_4]H_2$ and metatungstic acid $H_2W_4O_{13}$ (p. 495). Polyacids which contain one kind of radical, such as those just mentioned, are termed *isopolyacids*, but if one of the radicals is derived from another negative element the name *heteropolyacid* is applied (Rosenheim). The radicals of vanadic, tungstic and molybdic acids unite with radicals of other fairly strong acids, or with amphoteric metallic hydroxides, to form heteropolyacids. This property is a point of resemblance peculiar to these three acids. The acids usually known as phosphotungstic, phosphomolybdic, phosphovanadic, silicotungstic and -molybdic acids, arsenomolybdic acid and borotungstic acid are heteropolyacids. It is distinctive of heteropolyacids that a single radical of one of the acids is united with many, perhaps twelve, radicals derived from the second acid. The complex acids derived from molybdic, vanadic, tungstic and silicic acids are particularly numerous.

Constitution.—The structure of the heteropolyacids is still unsettled. This very large class of compounds presents great difficulties in analysis, for, owing to the size of the molecules, differences of a fraction of a per cent. correspond to a considerable variation of the molecular formula. A careful examination of the heteropolyacids and their salts must be made before a systematic classification can be drawn up. One of the most satisfactory theories was that due to Miolati,[2] which was based on Werner's co-ordination theory, and has been successfully developed by Rosenheim.[3] The Miolati-Rosenheim conception is used as a basis for the following account of these acids (*cf.* the classification of Rosenheim and Jänecke[4]).

[1] *Z. anorg. Chem.*, 1899, 21, 60.

[2] *J. prakt. Chem.* (2), 1908, 77, 417.   [3] *Z. anorg. Chem.*, 1910, 69 *et seq.*

[4] *Z. anorg. Chem.*, 1917, 100, 304.

According to Miolati, the typical acid atom of the heteropolyacid, *i.e.* the phosphorus atom in phosphoric acid, the arsenic atom in arsenic acid, etc., is to be regarded as a central atom or nucleus. This central atom is hydrated and attached to six oxygen atoms, thus H_7PO_6 (*i.e.* H_3PO_4, $2H_2O$); H_5IO_6 (*i.e.* HIO_4, $2H_2O$); H_8SiO_6 (*i.e.* H_4SiO_4, $2H_2O$) or H_9BO_6 (*i.e.* H_3BO_3, $3H_2O$). The oxygen is linked to the nuclear atom of P, I, Si or B in the same way that the molecules of ammonia are bound to the metal atom in the metallic ammines; the oxygen atoms can be wholly or partially substituted by radicals such as MoO_4, Mo_2O_7, WO_4, W_2O_7, VO_3, V_2O_6. Compounds of the following series are thus formed:

$$H_7\left[P(Mo_2O_7)_6\right] \quad H_7\left[P\overset{(Mo_2O_7)_5}{O}\right] \quad H_7\left[P\overset{(Mo_2O_7)_4}{O_2}\right] \text{ etc.}$$
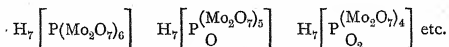
The greatest number of radicals that can be combined with the central atom is six. Compounds in which the co-ordination number equals six are said to belong to "limiting series" (Rosenheim), and if the whole of the oxygen has been replaced the term "saturated series" is applied. The maximum number of co-ordinated groups is not always present, as has been mentioned in dealing with other series of complex compounds; *e.g.* the following substance has a co-ordination number 4:

$$H_8\left[As\overset{(MoO_4)_3}{O}\right].$$
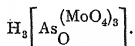
This compound does not belong to a limiting series, and is "unsaturated." The highest co-ordinated series are derived from unstable hydrated acids, but this is not unusual, as many unstable compounds are known which become more stable when forming part of a complex.

The reasons for the existence of so many of these heteropolyacids are the possibility of different central atoms, the variety of the co-ordinated acid radicals, the presence of different acid radicals in the same molecule and the varying degree of saturation.

The most important types of the compounds containing one of the groups Mo_2O_7 or W_2O_7 are:

$$R_{10}[H_2(W_2O_7)_6] \quad R_7[P(W_2O_7)_6] \quad R_7[As(W_2O_7)_6] \quad R_9[B(W_2O_7)_6]$$
$$R_{10}[H_2(Mo_2O_7)_6] \quad R_7[P(Mo_2O_7)_6] \quad R_7[As(Mo_2O_7)_6] \quad R_8[Th(W_2O_7)_6]$$
$$R_8[Si(W_2O_7)_6] \quad R_8[Sn(Mo_2O_7)_6] \quad R_8[Zr(Mo_2O_7)_6]$$
$$R_8[Si(Mo_2O_7)_6] \quad R_8[Ce(Mo_2O_7)_6] \quad R_8[Ti(Mo_2O_7)_6].$$
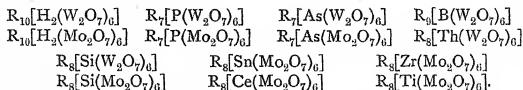
Other compounds contain different kinds of co-ordinated radicals; *e.g.* $R_7\left[P\overset{(V_2O_6)_3}{(Mo_2O_7)_3}\right]$; it would be inconvenient to give a full list of them. In the above examples, H, P, As, B, Th, Si, Sn, Ce, Zr and Ti occur as central atoms, P and As being the most common, and

then Si, B and H; there are also compounds in which tervalent iron, rhodium, chromium, quadrivalent platinum and other elements play the part of central atom.

Reference has been made to the gradual substitution of W_2O_7 radicals by oxygen; the process can only be continued until four Mo_2O_7 or W_2O_7 radicals are left. Apparently an isomeric change then takes place, the R_2O_7 groups splitting up into two RO_4 groups:

$$\left[As \genfrac{}{}{0pt}{}{(Mo_2O_7)_3}{O_3} \right] \quad \longrightarrow \quad \left[As(MoO_4)_6 \right].$$

The constitution of the intermediate members of the series is also ambiguous; e.g. the dioxy-compounds may be equally well represented by either of the formulae:

I. $\left[As \genfrac{}{}{0pt}{}{(Mo_2O_7)_4}{O_2} \right] H_7.$ II. $\left[As \genfrac{}{}{0pt}{}{(Mo_2O_7)_4}{(OH)_2} \right] H_5.$
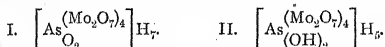
The existence of double radicals, W_2O_7, Mo_2O_7, and V_2O_6, is doubtful. The assumption has been made because, according to Werner's co-ordination theory, the co-ordination number is usually 6. The double radical hypothesis explains the occurrence of twelve MoO_3, WO_3 or $\frac{1}{2}V_2O_5$ radicals in one complex—a greater number has never been observed. Numerous attempts, however, have been made to find out whether one part of the complex is more closely attached to the central atom than another. Replacement of oxygen atoms by Mo_2O_7 groups has been experimentally observed in the series of compounds:

$R_2\left[As \genfrac{}{}{0pt}{}{(CH_3)}{O_3} \right]$ $R\left[As \genfrac{}{}{0pt}{}{(CH_3)_2}{O_2} \right]$ $\left[As \genfrac{}{}{0pt}{}{(C_6H_5)_3}{O} \right]$

Methyl arsenious acid. Cacodylic acid. Tri-phenyl arsenic oxide.
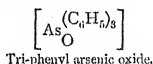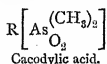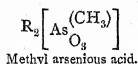
This affords a proof of the actual occurrence of these substitutions. There is also evidence of the existence of the simple groups MoO_4 and WO_4; e.g. the constitution $R_9H_6[M(MoO_4)_6]$, aq. and not $R_3\left[M \genfrac{}{}{0pt}{}{(H_2O)_3}{(Mo_2O_7)_3} \right]$, aq. has been given to one class of compound, though proof of this structure is too involved to be included here. Rosenheim gives the following examples of types of compounds which contain single radicals, MoO_4 and WO_4:

$R_5[I(MoO_4)_6]$ $R_6[Te(WO_4)_6]$ $R_9[Fe(MoO_4)_6]$ $R_9[Cr(MoO_4)_6]$
$R_5[I(WO_4)_6]$ $R_6[Te(MoO_4)_6]$ $R_9[Fe(WO_4)_6]$ $R_9[Al(MoO_4)_6]$

$R_9[Co(MoO_4)_6]$ $R_{10}[Ni(MoO_4)_6]$ $R_{10}[H_2(MoO_4)_6]$
$R_9[Rh(MoO_4)_6]$ $R_{10}[Cu(MoO_4)_6]$ $R_{10}[H_2(WO_4)_6]$
$R_{10}[Mn(MoO_4)_6].$
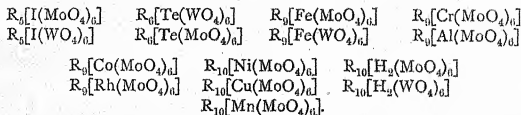
Examples of compounds with mixed radicals are:

$$R_{10}\left[H_2\genfrac{}{}{0pt}{}{(V_3O_6)_3}{(Mo_3O_7)_3}\right], aq. \qquad R_6\left[H_2\genfrac{}{}{0pt}{}{(V_2O_6)}{(Mo_2O_7)_3}\right] \text{ or } R_{10}\left[H_2\genfrac{}{}{0pt}{}{(V_2O_6)O_2}{(Mo_2O_7)_3}\right]$$

$$R_9\left[As\genfrac{}{}{0pt}{}{(VO_3)_2}{O_3}\right] \qquad R_8\left[As\genfrac{}{}{0pt}{}{VO_3}{O_3}\right] \qquad R_7\left[P\genfrac{}{}{0pt}{}{(V_2O_6)_3}{(Mo_3O_7)_3}\right]$$

$$R_7\left[P\genfrac{}{}{0pt}{}{V_2O_6}{(Mo_2O_7)_3}\right] \qquad R_8\left[Si\genfrac{}{}{0pt}{}{V_2O_6}{(W_2O_7)_5}\right] \qquad R_8\left[P\genfrac{}{}{0pt}{}{VO_3}{O_3}\right].$$
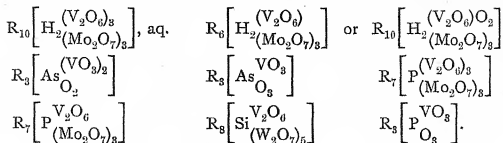
Probably more than two different acid radicals can be attached to the central atom. There are compounds which contain vanadium in different stages of oxidation, and some very complicated types are known; e.g. $18BaO$, V_2O_5, VO_2, $3P_2O_5$, $60WO_3$, $150H_2O$. These substances may contain solid solutions of the simple components.

The foregoing treatment gives a convincing explanation of the structure of many of these heteropolyacids, but it should be stated that there is no proof of the correctness of many of the formulae. The basicity of these acids is not easily determined. The well-known yellow ammonium phosphomolybdate was originally given the formula $(NH_4)_3PO_4.12MoO_3$. It was therefore regarded as a molecular compound of normal ammonium phosphate with MoO_3, and hence many of the most important acids were believed to be tribasic. This salt, however, always holds water of crystallisation, and Miolati's determinations of conductivity show that the parent acid is not tribasic, but at least septabasic, having the constitution $H_7[P(Mo_2O_7)_6]$. Ammonium phosphomolybdate is an acid salt, i.e. $(NH_4)_3H_4[P(Mo_2O_7)_6]$, aq. The addition of guanidine carbonate to free phosphomolybdic acid gives a salt: $(CN_3H_6)_7[P(Mo_2O_7)_6].8H_2O$, and septabasic silver and mercury salts have also been prepared (Rosenheim). Salts in which the whole of the available hydrogen of the acid is replaced are striking exceptions to the general rule; the guanidine salts can possibly be regarded as anomalous ammonium salts. The structure which has been suggested for the heteropolyacids agrees with the fact that the great majority of the salts are acid salts. As, however, silver and mercury ions are able to replace all the hydrogen atoms, it is probable that those atoms which are replaceable by Ag and Hg but not by alkalis are pseudo-acidic; the preceding formulae make no distinction in the hydrogen atoms. Moreover, they afford an incomplete explanation of a large number of compounds which have been prepared and analysed, while others can only be represented by very complicated formulae containing several nuclei. The compound $5R_2O_3.7V_2O_5.14WO_3.xH_2O$ serves as a good example:

$$R_{20}H_6\left\{\left[\genfrac{}{}{0pt}{}{(W_2O_7)_4}{(V_2O_6)_3}H_2\right]-W_2O_7-\left[\genfrac{}{}{0pt}{}{(W_2O_7)_4}{(V_2O_6)_3}H_2\right]-W_2O_7-\left[H_2\genfrac{}{}{0pt}{}{(W_2O_7)_4}{(V_2O_6)_3}\right]\right\}.$$
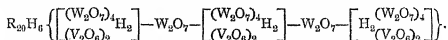
According to this formula, an acid salt exists containing three nuclei connected by two (W_2O_7) groups. Copaux first proposed the use of two hydrogen atoms as a nucleus.[1] If the nucleus of water is taken as $(H_2O)_6$ becoming, by isomeric change, $H_{10}[H_2(O)_6]$, a kind of "aquo-acid" results, in which the oxygen atoms can be replaced by the radicals W_2O_7 and Mo_2O_7, and the outside hydrogen atoms by metals. Formulae are thus obtained which explain clearly the structure of certain isopolyacids, e.g. the metatungstates (I.), tetramolybdates (II.), octomolybdates (III.) (cf. p. 513):

I. $R_6H_4[H_2(W_2O_7)_6]$. II. $R_6H_4[H_2(Mo_2O_7)_6]$. III. $R_9H_7[H_2(Mo_2O_7)_6]$.

These salts are termed "aquates," since the water acts as the "nuclear acid."

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[1] Ann. Chim. Phys. (8), 1906, 7, 118; 1909, 17, 217; 1912, 26, 22.

The conception is, however, artificial, and it would be better to halve the formulae. Then the co-ordination number would be less than 6, which is not unlikely with hydrogen as the central atom.

A serious objection to the formulae given above is that actually the double ions (Mo_2O_7) and (W_2O_7) cannot be detected in solution; and if the possibility of the existence of these configurations is questioned the whole of the above formulae become very doubtful. The fact that these groupings do not exist in the free form, however, does not exclude the possibility of their stability in a larger complex, and it would be premature to suggest that the Rosenheim-Miolati formulation should be given up completely. It must here be mentioned that the calculations of L. Pauling [1] indicate that from a steric point of view a configuration is possible in which the double molecule is not introduced. In the complex compounds which contain 12 MoO_4 or WO_4 groups, distorted octahedra are formed by 12 of the oxygen atoms occupying the corners. The other 36 atoms which are not joined together either carry a negative charge or have a hydrogen atom attached to them. The neutral structures thus formed are stabilised by a central group $(RO_4)'''$, in which R may be either H_2^{II}, B^{III}, Si^{IV}, P^V, or As^V. The formulae thus obtained are as follows :

$$H_6[H_2O_4W_{12}O_{18}(OH)_{36}] \qquad H_5[BO_4W_{12}O_{18}(OH)_{36}]$$
$$H_4[SiO_4W_{12}O_{18}(OH)_{36}] \qquad H_3[PO_4W_{12}O_{18}(OH)_{36}]$$

It will be noted that they are different from and in many ways superior to those of Rosenheim; they utilise the maximum basicity in agreement with experimental observations, and the known high content of water is also in agreement with these formulae. Similar possible formulae can be written for the other series of heteropolyacids.

Hoard [2] and Keggin [3] have shown by X-ray analysis that the 12-heteropolyacids have structures typified by $H_3[PO_4(W_{12}O_{36})]$. $5H_2O$. The complex anion is approximately spherical. The P atom is at the centre, surrounded by 4 oxygen atoms tetrahedrally arranged. Each of these 4 is common to groups of 3 octahedra ; at the centre of each octahedron is a tungsten atom (i.e. 12 WO_6 groups in all). In each WO_6 group one oxygen atom is shared with P, two are shared with W atoms in its own group of 3 octahedra, two are shared with W atoms in other groups, and one is unshared. Signer and Gross [4] showed this structure to be present in the hydrated forms of $H_5[BO_4(W_3O_9)_4]$, $H_4[SiO_4(W_3O_9)_4]$ and metatungstic acid, $H_6[H_2O_4(W_3O_9)_4]$. Illingworth and Keggin [5] arrive at analogous structures for

phospho-molybdic acid $H_3[PO_4(Mo_3O_9)_4]$
arseno-molybdic acid $H_3[AsO_4(Mo_3O_9)_4]$
silico-molybdic acid $H_4[SiO_4(Mo_3O_9)_4]$
mangani-molybdic acid $H_4[MnO_4(Mo_3O_9)_4]$
titani-molybdic acid $H_4[TiO_4(Mo_3O_9)_4]$
germani-tungstic acid $H_4[GeO_4(W_3O_9)_4]$
arseni-tungstic acid $H_3[AsO_4(W_3O_9)_4]$.

Also, all compounds previously formulated as $H_8[X(Mo_2O_7)_6]$ are probably $H_4[XO_4(Mo_3O_9)_4]$ (X = Ce, Th, Zr, Sn, Ge). Heteropolyacids derived from H_5IO_6 and H_6TeO_6, e.g. $Na_5[I(MoO_4)_6]13H_2O$ and $(NH_4)_6[Te(MoO_4)_6]7H_2O$, are probably of a different type.

J. S. Anderson [6] suggests a structure for the 6-heteropolyacids and the related

[1] J. Amer. Chem. Soc., 1929, 51, 2868.   [2] Z. Krist., 1933, 84, 217.
[3] Nature, 1933, 131, 908 ; Proc. Roy. Soc., 1934 [A], 144, 75.
[4] Helv. Chim. Acta, 1934, 17, 1076.   [5] J. Chem. Soc., 1935, 575.
[6] Nature, 1937, 140, 850.

paramolybdates and paratungstates. Six MoO_6 octahedra are arranged in a hexagonal Mo_6O_{24} annulus by each sharing two corners of neighbouring octahedra. The central space thus left is of the same shape as the MoO_6 octahedron and accommodates a 6-coördinated cation; thus giving the paramolybdate structure as $R_6[Mo(Mo_6O_{24})]$ corresponding to the 6-molybdoperiodate, $R_6[I(Mo_6O_{24})]$. J. H. Sturtevant[1] has shown that ammonium paramolybdate is correctly formulated as

$$3(NH_4)_2O \cdot 7MoO_3 \cdot 4H_2O, \ i.e. \ (NH_4)_6 \ [Mo_7O_{24}] \ 4H_2O.$$
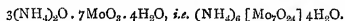
Nomenclature.—The older and more familiar names for these compounds, *e.g.* phosphotungstic acid, silicomolybdic, etc., in which the nuclear acid is named first and the co-ordinated acid second, are neither strictly accurate nor sufficiently general. They are sometimes useful on account of their brevity. The new nomenclature introduced by Rosenheim and Koppel is logical and exhaustive, but rather cumbersome. It will be used where necessary, and a few examples are quite sufficient to explain the system :

$H_7[P(Mo_2O_7)_6]$, aq.
12-Molybdo-phosphoric acid.

$H_7[AsO(Mo_2O_7)_6]$, aq.
10-Molybdo-arsenic acid.

$3K_2O, P_2O_5, 21WO_3, 31H_2O$
Potassium-21-tungsto-2-phosphate.
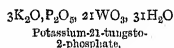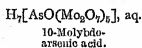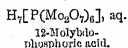
Preparation and Properties.

—The salts of the heteropolyacids are produced by mixing the components in acid or neutral solution. The preparation of yellow ammonium phosphomolybdate by the action of a phosphate on a nitric acid solution of ammonium molybdate is well known. The compounds are also obtained by heating a normal salt of the acid which supplies the central atom with the anhydride of the co-ordinated acid ; *e.g.* 12-tungsto-phosphate, $3R_2O$, P_2O_5, $24WO_3$, aq., is produced when a boiling solution of alkali phosphate is saturated with tungsten trioxide. Similarly, molybdo-vanado-phosphates,

$$R_7\left[P\begin{matrix}(V_2O_6)_3\\(Mo_2O_7)_3\end{matrix}\right], \text{ aq.,}$$

are prepared either by the addition of phosphoric acid to a mixture of alkali vanadate and molybdate solutions, or by warming molybdo-phosphates with V_2O_5 or with vanadates; in fact, by any method which allows the component salts to react with one another in acid solution. All the maximum co-ordinated compounds can be produced by these methods. The preparation of those belonging to unsaturated series is more difficult. These compounds can sometimes be produced from solutions containing the theoretical quantities of the components. Another method is to decompose the compounds which are fully co-ordinated. These are partly broken up when dissolved, with the formation of equilibrium mixtures of anhydrides, for the stability of the complexes is not very great. Sufficient hydroxyl ions to decompose the polyacids are formed as the result of normal hydrolytic action of the water, but the addition of alkali hydroxide or carbonate accelerates the reaction. Hence yellow ammonium phosphomolybdate dissolves rapidly in alkalis, forming the alkali molybdate. These saturated polyacids are extremely sensitive to the influence of OH′ ions, and by the gradual introduction of these

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[1] *J. Amer. Chem. Soc.*, 1937, 59, 630.

ions the decomposition proceeds in stages. The following molybdo-phosphates have been described:

$3R_2O \cdot P_2O_5 \cdot 24MoO_3$, aq.
$3R_2O \cdot P_2O_5 \cdot 22MoO_3$, aq.
$3R_2O \cdot P_2O_5 \cdot 20MoO_3$, aq. } Yellow
$3R_2O \cdot P_2O_5 \cdot 18MoO_3$, aq.
$3R_2O \cdot P_2O_5 \cdot 17MoO_3$, aq.

$(2\frac{1}{2}$ and $3)R_2O \cdot P_2O_5 \cdot 5MoO_3$
$2R_2O \cdot P_2O_5 \cdot 2\frac{1}{2}MoO_3$ } White
$R_2O \cdot P_2O_5 \cdot 2MoO_3$
etc.
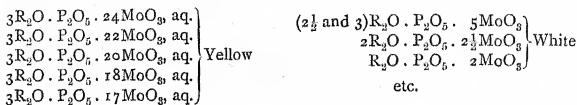
The yellow compounds are said to contain Mo_2O_7 radicals, and the white, or less acid salts, the MoO_4 radical. It must not be assumed that all these substances are definite chemical compounds. They are, however, quite as well defined as the different series of salt hydrates. Completely or partially isomorphous mixtures of definite compounds are perhaps present. It is probable that only the maximum co-ordinated bodies are true chemical individuals in the sense that they obey the law of constant proportions, and that the free interatomic space of the unsaturated substances is filled up to a varying degree by MoO_3 groups. Adsorption of uncombined MoO_3 groups by molecules containing a large number of these radicals may also play a part. The molecules of the adsorbing compound must possess free space between their atoms if adsorption is to be possible. Hence the phenomenon does not occur with maximum co-ordinated compounds.

Isomorphism among the heteropolyacids is an interesting subject. The replacement of Mo_2O_7 by V_2O_6 or W_2O_7 frequently causes no change in the crystalline form, especially with saturated compounds, and even the central atom can be changed without affecting the crystal shape, provided the basicity of the acid is unaffected. Alkali metals in the salts can even be replaced by alkaline earth metals and heavy metals without disturbance of the crystalline form. The following six acids form two series, made up of three pairs:

$H_7[P(Mo_2O_7)_6]$ $H_8[Si(Mo_2O_7)_6]$ $H_{10}[H_3(W_2O_7)_6]$
$H_7[P(W_2O_7)_6]$ $H_8[Si(W_2O_7)_6]$ $H_9[B(W_2O_7)_6]$.
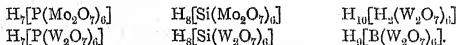
The two series are isomorphous; the one set crystallising with 28 mols. H_2O in cubic or tetragonal crystals, the other with 22 mols. H_2O in large rhombohedra. The slight effect of replacing one positive radical by another is illustrated by the isomorphism of the three compounds:

$H_7[P(W_2O_7)_6],19H_2O$ $Na_3H_4[P(W_2O_7)_6],19H_2O$ $Ba_3H_8[P(W_2O_7)_6]_2,44H_2O$.
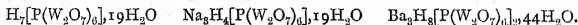
Evidently the crystal lattice is determined by the number of co-ordinated groups; these form the framework on which the rest of the molecule is built. The space between the central atom and the positive radical is so filled up with the co-ordinated groups that the crystal lattice must necessarily be very compact (see p. 504). The regular system fulfils this condition best, and the polyacids usually crystallise in one of these forms. Similarly the alums, which are packed with molecules

of water, also assume the regular shape. Other examples are the hexammines and the chloroplatinates (K_2PtCl_6). The heteropolyacids, especially the closely packed compounds with six co-ordinated groups, give large well-defined crystals, unlike organic compounds of high molecular weight, which are often amorphous. The free acids and alkali salts, in particular, crystallise well.

The heteropolyacids themselves are fairly strong acids. This property confirms the work of Abegg and Bodländer, according to which the complex acid is always stronger than the nuclear acid (*cf.* p. 617), and even these acids are not as a rule very weak. The free heteropolyacids are very soluble. They can be obtained either from a mixture of the components, or by precipitation from a solution of one of the salts. There is a third method much used for 12-tungsto-phosphoric acid and similar compounds—the ammonium salt is treated with warm *aqua regia*, which completely oxidises the ammonia. A characteristic property of the heteropolyacids is their solubility in ether, so much so that even when merely kept over this solvent they often dissolve. When a concentrated aqueous solution is shaken with ether the liquid separates into three layers (*cf.* meta-tungstic acid, p. 495). The upper one contains the excess of ether, the middle is mainly water, while the lower layer consists of an ethereal solution of the acid. Probably, however, this liquid is not a simple solution, but contains a complex compound of the acid with ether, similar to the ether compounds of ferrocyanic acid (*cf.* p. 266). The vapour pressure of the complex compounds is so great that they cannot be isolated.

As the stability of the heteropolyacids is not very great, aqueous solutions contain equilibrium mixtures of acids of a larger number of co-ordinated groups with those containing a smaller number. The equilibria are displaced by heat, and frequently compounds other than those which were dissolved crystallise out. This behaviour is similar to that of the chromates (p. 477) and the vanadates (p. 493), which are also salts of polyacids.

Although the heteropolyacid salts are easily soluble they crystallise well. Owing to this great solubility, solutions of very high specific gravity can be prepared (*e.g.* cadmium borotungstate and free 12-tungsto-phosphoric acid), and are useful for separating minerals of different densities. Reference has been made to the slight solubility of the silver and mercury salts. When precipitated they are amorphous, but gradually become crystalline on standing, or when heated. The guanidine salts are also slightly soluble. The alkaline earth and heavy metal salts are nearly all very soluble, but the alkali salts, especially those of caesium, dissolve less readily. The ammonium salts are often still less soluble. The ammonium compounds of 12-molybdo-phosphoric acid, 12-tungsto-phosphoric acid, and

of the corresponding arsenic derivatives, are characteristic, and are used as a test for phosphates and arsenates. The heteropolyacids are extremely delicate reagents for albumin and many of the alkaloids. Albumin is precipitated as a thick, amorphous mass from very dilute solutions by phosphotungstic acid and similar compounds. By this method, also, one part of quinine in 600,000 parts can be detected. Characteristic precipitates are also produced with the cobalt and chromium ammines, e.g. $[Co(NH_3)_6]X_3$.

The individual compounds are too numerous to be described separately, but a few classes may be examined in greater detail, and for this purpose the heteropolyarsenates and phosphates are selected—other types of compound show many similarities to them.

Of the *molybdoarsenates* the following acids have only four co-ordinated groups:

$$\text{I. } H_3\left[As{(MoO_4) \atop O_3}\right] \qquad \text{II. } H_3\left[As{(MoO_4)_2 \atop O_2}\right] \qquad \text{III. } H_3\left[As{(MoO_4)_3 \atop O}\right].$$
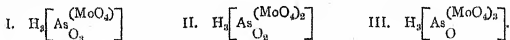
These are derived from arsenic acid by the successive replacement of oxygen atoms by MoO_4 groups. They are produced by dissolving the theoretical quantity of MoO_3 in a solution of arsenate, with subsequent evaporation; the free acid III is obtained by warming arsenic acid with excess of MoO_3 until the saturation point is reached. These compounds are white and not very stable. Only the alkali salts of I and II are known, but many salts of III have been prepared by neutralising the free acid. III is a stronger acid than arsenic acid, for the normal salts are neutral to phenolphthalein, whereas the normal arsenates react alkaline owing to hydrolysis.

The following acids have the maximum number of co-ordinated groups:

$$\text{IV. } H_5\left[As{(Mo_2O_7)_4 \atop (OH)_2}\right], \text{aq.} \qquad\qquad \text{V. } H_{12}\left[As_2{(Mo_2O_7)_9 \atop O_2}\right], \text{aq.}$$

$$\textit{i.e. } 7H_2O,As_2O_5,16MoO_3, \text{aq.} \qquad\qquad 6H_2O,As_2O_5,18MoO_3, \text{aq.}$$

$$\text{VI. } H_7\left[As{(Mo_2O_7)_5 \atop O}\right], \text{aq.} \qquad\qquad \text{VII. } H_7\left[As(Mo_2O_7)_6\right], \text{aq.}$$

$$\textit{i.e. } 7H_2O,As_2O_5,20MoO_3, \text{aq.} \qquad\qquad 7H_2O,As_2O_5,24MoO_3, \text{aq.}$$
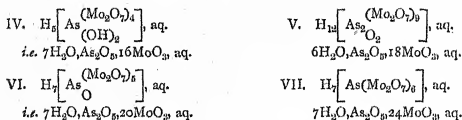
Compound VII is saturated. IV has not been completely examined, and its constitution is uncertain. The colour, which is white, is contrary to the structure given, for compounds containing Mo_2O_7 groups are usually yellow. Substance V possesses two nuclei and may be represented thus:

$$H_6\left[{(Mo_2O_7)_4 \atop O}As—Mo_2O_7—As{(Mo_2O_7)_4 \atop O}\right]H_6.$$
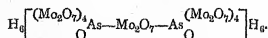
The free acid and its normal and acid salts are well known. It is prepared by saturating a solution of sodium arsenate with molybdic acid, decomposing the product with strong hydrochloric acid and extracting with ether (cf. p. 507); it is soluble in water. The acid crystallises in two forms: above 8°, as red crystals with 24 mols. water; below 8°, as yellow crystals with 34 mols. water. Acid salts of the type $R_6H_6\left[As_2{(Mo_2O_7)_9 \atop O_2}\right]$, aq. show a greater range of colour. They are obtained by saturating alkali arsenates with molybdic acid, and are also very soluble. When kept, their appearance changes; thus the deep yellow crystals of the sodium compound slowly become white and fall to powder—an effect which is reversible. These

changes may be due to variation in the quantity of combined water, or to more fundamental changes of structure. Many of the acid salts are well-crystallised. When their solutions are treated with metallic salts precipitates are thrown down, of which the composition often corresponds to that of normal salts. This affords a convincing proof that the acid actually has twelve replaceable hydrogen atoms. These normal salts are produced by precipitation of the silver, thallous, caesium and guanidine compounds.

The guanidine salt is the only derivative of compound VI which has been prepared. The free acid is unknown. This substance separates as deep yellow plates when a solution containing 1 mol. arsenic acid and 12 mols. of normal guanidine molybdate is acidified with hydrochloric acid; the initial product is an acid salt, in which only three out of the seven hydrogen atoms are replaced by guanidine, but it can be converted to the normal salt by treatment with guanidine carbonate.

Compounds belonging to type VII are the best known of this series of acids. Ammonium arseno-molybdate separates in yellow octahedra when a solution of a soluble arsenate containing excess of molybdate is acidified with nitric acid. The fact that it dissolves in ammonia illustrates its sensitiveness towards alkalis. The potassium salt has also been prepared, but not the free acid.

Organic radicals can also replace the oxygen atoms of the oxy-molybdo-arsenates. The following compounds have been obtained:

$$R_6\left[As\frac{CH_3}{(Mo_3O_7)_3}\right] \qquad R_6\left[As\frac{C_6H_5}{(Mo_3O_7)_3}\right] \qquad R_9\left[As\frac{C_6H_4NH_2}{(MoO_3)_9}\right]$$

$$R_3H\left[As(Mo_3O_7)_3\frac{(CH_3)_3}{(OH)_3}\right] \qquad R_3H\left[As(Mo_3O_7)_3\frac{(C_6H_5)_3}{(OH)_3}\right].$$
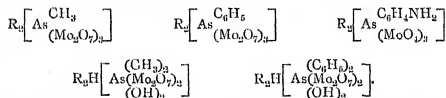
A few examples will suffice to illustrate the complex arsenates derived from sulphuric, selenic, telluric and chromic acids:

$$R_2H\left[As\frac{SO_4}{O_3}\right] \qquad R_2H\left[As\frac{SeO_4}{O_3}\right] \qquad R_2H\left[As\frac{TeO_4}{O_3}\right] \qquad R_2H\left[As\frac{(CrO_4)_2}{O_3}\right]$$

$$R_5H_2\left[As\frac{(SO_4)_4}{O_2}\right] \qquad R_5\left[As(CrO_4)_4\right].$$
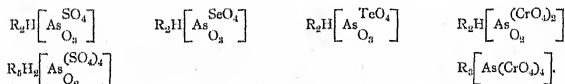
A description of the very numerous *tungsto-* and *vanado-phosphates* will virtually include the arsenic compounds also, as these are very similar to the phosphates, but less varied.

Two kinds of vanado-phosphates are known: first, the violet-red saturated derivatives, also termed the purpureo series, of the formula $R_7[P(V_2O_6)_6]$, with which may be included the unsaturated type, $R_6H_2[PO(V_2O_6)_5]$; secondly, the bright yellow crystalline luteo compounds are of the general formulae:

$$R\left[P\frac{(VO_3)_2}{O_2}\right] \qquad R_2\left[P\frac{VO_3}{O_3}\right].$$

The purpureo salts are produced by saturating aqueous solutions of the alkali phosphates with V_2O_5, while the luteo salts are made by addition of excess of phosphoric acid to the alkali vanadates. The only free acid that has been prepared has the formula $H_2[PO_3(VO_3)],4\frac{1}{2}H_2O$, and crystallises in golden-yellow plates. There are a great many series of tungsto-phosphates; they strongly resemble the molybdo-phosphates and -arsenates. They are also very stable compounds.

Very little is known of the compounds analogous to the molybdo-arsenates which were discussed above. Possibly the unsaturated substances containing only a small percentage of tungstic acid do not exist. Of the compounds rich in tungstic acid,

the saturated series, $R_7[P(W_2O_7)_6]$, aq., are the most easily prepared. The method consists either in acidifying with hydrochloric acid an alkali phosphate solution containing an excess of tungstate or in adding tungsten trioxide to a solution of the alkali phosphate and heating till the liquid becomes saturated. The guanidine compound is the only normal salt known. The majority of the salts are formed by replacement of three or less hydrogen atoms. The potassium and ammonium tetra-hydrogen salts are slightly soluble, but the sodium salt dissolves more readily. The free acid is very stable, and is obtained by decomposition of the sodium salt with hydrochloric acid and extraction with ether. Various crystalline hydrates are obtained, according to the temperature of reaction. This acid is excessively soluble, and the solution is of importance on account of its great density.

Isopolyacids.—Many molybdates, tungstates, vanadates, silicates, etc., may be regarded as salts of polyacids. The constitutional formulae employed in the following description of these salts are open to some objections; they have the same basis as the formulae used for the hetero-acids.

The vanadates have not yet been sufficiently examined for a systematic classification to be made; the silicates are described on p. 825 *et seq.* The structure of the tungstates is simpler than that of the molybdates (*cf.* p. 512).

Tungstates.—The tungstates fall into two main groups. The normal tungstates, R_2O, WO_3, the paratungstates of the type $5R_2O$, $12WO_3$, aq., or $3R_2O$, $7WO_3$, aq., and the bi- and tri-tungstates, R_2O, $2WO_3$, and R_2O, $3WO_3$, belong to the first class. The second class comprises the metatungstates of the molecular formula R_2O, $4WO_3$, aq., and perhaps the higher acid salts, *e.g.* the octa-tungstates, R_2O, $8WO_3$. The two groups are distinguished by the different products produced by the addition of acid; the first gives the insoluble yellow colloidal tungstic acid (*cf.* p. 495); the second is converted to the soluble crystalline metatungstic acid (p. 495). There are many other important differences. Compounds of the first class are able to influence considerably the optical rotation of organic acids, *e.g.* tartaric acid, owing to the formation of complex compounds. Those of the second class do not possess this property. The former are usually produced at room temperatures, the latter from boiling solutions. Only the alkali and magnesium salts of the first group are soluble, the acid salts being less soluble than those derived from the type R_2O,WO_3. The majority of the alkaline earth and heavy metal salts of the second group are easily soluble. In solution the normal tungstates react strongly alkaline, the paratungstates neutral, while the metatungstates have a weakly acid reaction.

Cooling curves of a fused mixture of Na_2O and WO_3 prove the existence only of the compounds Na_2O,WO_3 and $Na_2O,2WO_3$. The salt $Na_2O,5WO_3$ may be formed, but there is no trace of para- or meta-tungstates. This result agrees with the fact that these compounds contain water of crystallisation, and so can only be produced from solutions. Hence the para- and meta-tungstates are decomposed by

heat; *e.g.* sodium paratungstate dried above 250° leaves a residue which is a mixture; Na_2O,WO_3 can be washed out with water and the insoluble $Na_2O,4WO_3$ remains behind.

The First Group.—The normal tungstates of the alkali metals are obtained by fusing the theoretical quantities of base and WO_3 together, and then allowing the melt to crystallise. The salts of the heavy metals are precipitated from solution by the method of double decomposition. The precipitates are amorphous. If the solution of the normal alkali salt is neutralised with acid and evaporated the paratungstates crystallise. They have the formulae $5R_2O,12WO_3$, aq. (the K and NH_4 salts contain 11 mols. H_2O, the Na salt 28, 25 and 21 mols.) or $3R_2O,7WO_3$, aq. (K and NH_4 salts contain 6, the Na salt 16 or 21 mols. H_2O). It is impracticable to decide which is the correct formula by analysis, because the theoretical percentage figures, corresponding to the two alternatives, are very nearly identical. Assuming the ratio of base to acid to be 3 : 7, the probable formula would be $R_6[W(WO_4)_6]$, although there is some evidence in favour of other structures, especially as the formula quoted does not explain why the paratungstates are so strongly combined with water, and can only be prepared from aqueous solution. (See also p. 504.)

The acid tungstates of the first group are ill-defined—the alkali salts are only slightly soluble.

The Second Group.—The metatungstates are the most important members of this class. They are produced by boiling paratungstates with yellow tungstic acid, until a drop of the filtered liquid no longer gives a precipitate with acids. Free metatungstic acid is very soluble in water. Metatungstates are perhaps produced when melts of the empirical composition $R_2O,4WO_3$ are heated for a very long time with water at 120°. They have the formula R_2O,WO_3, aq. The water is chemically combined, for when it is expelled by heat the solubility and other properties of the residue are entirely changed. Part of the water is retained at a temperature above 100°. According to Copaux's theory[1] these substances are "aquates" (*cf.* p. 503), the acid having the composition $H_{10}[H_2(W_3O_7)_6]$. This theory explains the isomorphism of the metatungstates with the following group of acids:

$$H_9[B(W_2O_7)_6] \qquad H_6[Si(W_2O_7)_6] \qquad H_7[P(W_2O_7)_5]$$
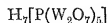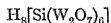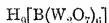
(*cf.* p. 506). There are other similarities between these compounds, including method of preparation, solubility, crystal properties, and the fact that the acids can be isolated from solution by extraction with ether. The ten hydrogen atoms are not all replaceable, the acids behaving as though they were hexabasic. Hence the salts are of the type $R_6H_4[H_2(W_2O_7)_6]$, and are produced from acid solutions. A more satisfactory formula for the metatungstates, however, is obtained by

[1] *Ann. Chim. Phys.* (18), 1909, 17, 207.

halving that proposed by Copaux (*cf.* p. 503). Most of these compounds are crystalline, but in order to get well-defined crystals the liquids must be allowed to evaporate in the cold; when hot solutions are evaporated, syrups and vitreous residues are formed. The free acid is isomorphous with its Na, K, NH_4, Mn and Cd salts, and forms large, tetragonal crystals, almost like octahedra (see p. 506). The metatungstates are not precipitated by acids, but are converted by alkalis into tungstates of the first group. Some little-known hexa- and octatungstates probably belong to this group.

Molybdates (for molybdic acid see p. 496).—The molybdates are similar in many of their properties to the tungstates, but the types are more numerous. The molybdates can also be arranged in two groups, which, however, are less sharply distinguished from each other. In the first group the ratios of metallic oxide to MoO_3 are 1 : 1, 1 : 2, 3 : 7 (or 5 : 12), 2 : 5, 1 : 3 and 1 : 16; in the second group the ratios are analogous to those of the metatungstates, viz. 1 : 4 and 1 : 8. Molybdates formed by direct combination of the fused oxides always belong to one of the types 1 : 1 or 1 : 2; the others can be prepared only from aqueous solutions. These solutions, like those of chromates, vanadates and tungstates, contain mixtures of different types in chemical equilibrium with one another, and sometimes compounds, other than those which were dissolved, crystallise out. For example, when alkali hydroxides are saturated with MoO_3, the solutions contain tetramolybdates, but on crystallisation trimolybdates separate and the mother liquor contains higher acid salts. Sometimes a salt more acidic than the one dissolved crystallises, and then less acidic salts are left in solution. Concentrated solutions of the paramolybdates [3 : 7] are unstable, and deposit trimolybdates. Salts which crystallise out sometimes have the same composition as those in solution. Salts of type 1 : 1 can be prepared by fusing together theoretical quantities of the components and recrystallising from water. The types 3 : 7, 1 : 4 and 1 : 8 are obtained when the calculated quantities of hydrochloric acid are added, either to the fused mass (of composition 1 : 1) or to a solution of a simple molybdate, and the liquid evaporated. The type 1 : 16 is made by adding a large excess of acid. The paramolybdates are stable under a fairly wide range of conditions, so that it is unnecessary that the acidification should be theoretically accurate ; *e.g.* the ammonium salt is deposited from strongly ammoniacal solutions. $(NH_4)_2MoO_4$ can only be obtained from concentrated ammoniacal solutions, and easily loses ammonia, while $3(NH_4)_2O$, $7MoO_3$, $4H_2O$ is quite stable in air.

Remarkable progress in our knowledge of the existence and structure of the molybdates has resulted from the application of physico-chemical methods by Jander, Jahr and Heukeshoven,[1] who have also applied

¹ *Z. anorg. Chem.*, 1930, 194, 383.

like methods to the tungstates. They have determined the pH at which the various molybdates exist, using optical methods, electrometric titration and the rate of diffusion as criteria of the size of the anions. According to their results the number of MoO_3 groups in these salts is even greater than is assumed in the Rosenheim formulae. For example, the "dimolybdates" contain three MoO_3 groups, the "octomolybdates" twelve. In the following table the new and old formulae of the sodium molybdates are compared:

Empirical Formula.	Usual Name.	Rosenheim's Formula.	Jander's Formula and Name.
Na_2MoO_4, 2 aq.	Normal molybdate	......	$Na_2[MoO_4]$, 2 aq. sodium monomolybdate
$Na_2Mo_3O_7$, 6 aq.	Dimolybdate	$Na_6H_4[H_2(MoO_4)_6]$ 15 aq.	$Na_6[HMo_3O_{11}]$ 9 aq. trisodium trimolybdate
$5Na_2O$, $12MoO_3$, aq.	Para-molybdate	$Na_5H_6[H_2(MoO_4)_6]$ 15·5 aq.	$Na_5[HMo_6O_{21}]$ 18 aq. pentasodium hexamolybdate
$Na_2[Mo_3O_{10}]$ 7 aq.	Trimolybdate	$Na_4H_6[H_2(MoO_4)_6]$ 10 aq.	$Na_4[H_2Mo_9O_{91}]$ 13 aq. tetrasodium hexamolybdate
$Na_2[Mo_4O_{13}]$ 6 aq.	Meta-molybdate	$Na_6H_4[H_2(Mo_2O_7)_6]$ 21 aq.	$Na_6[H_2Mo_6O_{21}]$ 10·5 aq. trisodium hexamolybdate
$Na_2[Mo_6O_{19}]$ 17 aq.	Octa-molybdate	$Na_3H_7[H_2(Mo_2O_7)_6]$ 21 aq.	$Na_3[H_7Mo_{12}O_{41}]$ 22 aq. trisodium dodecamolybdate
$Na_2[Mo_{10}O_{31}]$ 6 aq.	Deca-molybdate	......	$Na_5[H_7Mo_{24}O_{78}]$ 12 aq. pentasodium ikositetramolybdate
$Na_2[Mo_{16}O_{49}]$ 9 aq.	16-molybdate	......	$Na_3[H_2Mo_{24}O_{7n}]$ 9 aq. trisodium ikositetramolybdate

All the molybdates of types 1 : 1, 1 : 2, 1 : 3, and 1 : 4 are insoluble, except the alkali and magnesium salts. The alkaline earth salts of the octamolybdates are also soluble, but even the alkali salts of the type 1 : 16 are soluble only with difficulty. The alkali salts belonging to the 1 : 10 series are peculiar. They exist in two forms: a very soluble, highly hydrated one and an almost insoluble, slightly hydrated modification. The first form can be converted into the second by warming the solution, but the reverse change does not take place on cooling.

According to the researches of Rosenheim and Felix[1] the tetra- and the octamolybdates are analogous to the metatungstates (cf. p. 511). The tetramolybdates are exactly similar, having the composition $R_6H_4[H_2(Mo_2O_7)_6]$, while the octamolybdates can be formulated: $R_3H_7[H_2(Mo_2O_7)_6]$. The reasons for assuming these formulae are similar to those given in discussing the structure of the metatungstates (p. 503), and the basis of this formulation is weakened if Jander's formulae are assumed to be correct. The octamolybdates are exceptionally well crystallised. Both classes coagulate albumin, an indication of their complex nature. The constitution of the paramolybdates is still very uncertain. It has yet to be ascertained

[1] *Z. anorg. Chem.*, 1913, 79, 292.

which of the two types of formulae, the $3:7$ or $5:12$, is correct. Assuming the first formula, the potassium and ammonium salts crystallise with $4H_2O$, while according to the second they combine with seven molecules of water. The following constitutions have been proposed:

$$R_6[Mo(MoO_4)_6] \quad \text{or} \quad R_5H_5[H_2(MoO_4)_6].$$
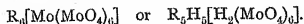
X-ray evidence is in favour of the former (pp. 503–505).

The ordinary molybdate of commerce is ammonium paramolybdate, which is obtained as large, transparent, six-sided prisms, stable in air; when the crystals are dried below $200°$ a new salt is formed. The trimolybdates occur as masses of crystalline needles, fairly soluble in water. The $1:16$ series of molybdates are similar to white molybdic acid in appearance.

Per-acids of the Metals

The acids of this series react with hydrogen peroxide in accordance with the reversible reaction $X.OH + H_2O_2 \rightleftharpoons X.O.OH + H_2O$. The OH group (and sometimes more than one of them) can thus be replaced by the $O.OH$ group. When equilibrium is reached the formation of the per-acid XOOH is as a rule practically complete. The per-acids under discussion are comparable with those of titanium, zirconium and thorium (p. 843), and also with perphosphoric acid and Caro's acid. All the acids which have been described in these two chapters give per-acids, with the exception of $HMnO_4$; it is possible that even this acid forms a very unstable per-acid (cf. p. 408). The decomposition of the perchromic and pervanadic acids is similar in principle, but takes a longer time. Perchromic acid occupies an exceptional position. Sexavalent chromium possibly becomes septavalent in the per-acid, while the valencies of the other metals are the same in the per-acid as in the normal acid. The perchromates are distinguished from the salts of the other per-acids by being well crystallised.

Perchromic Acids.—There are two kinds of perchromates: red salts of the formula M_3CrO_8 [I., Ia. or Ib.], and blue salts which possess the formula $MCrO_6$ [II. or IIa.].[1] The latter sometimes contain one molecule of hydrogen peroxide of crystallisation, their formula then becoming MH_2CrO_7. It is not necessary to regard this as a third type [III.], for it depends entirely on the nature of the base whether H_2O_2 of crystallisation is present or not. The structures assigned to the three types were:

I. $\quad \begin{matrix} O \\ O \end{matrix}\!\!>\!\!Cr\!\!\leftarrow\!\!\begin{matrix} O.OM \\ O.OM \\ O.OM \end{matrix}$ 　　II. $\quad \begin{matrix} O \\ O \end{matrix}\!\!>\!\!Cr\!\!<\!\!\begin{matrix} O.OM \\ O \end{matrix}$ 　　III. $\quad \begin{matrix} O \\ O \end{matrix}\!\!>\!\!Cr\!\!<\!\!\begin{matrix} O.OM \\ O.OH \\ OH \end{matrix}$
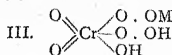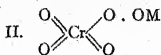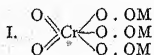
[1] Wiede, *Ber.*, 1897, **30**, 2178; Riesenfeld and collaborators, *Ber.*, 1905, **38**, 1885, 3380, 3578, 4068; 1908, **41**, 2826, 3536.

but other views have been put forward. Gleu[1] formulates the red perchromates as $M_3[Cr(O_2)_4]$, namely Ia.

$$O\Big\rangle Cr \Big\langle^{O.O.M}_{O.O.M}$$, containing

quinquevalent chromium; the magnetic susceptibility of K_3CrO_8 supports this view.[2] Rosenheim, Hakkiand and Krause[3] use the

formula Ib.

$$O=Cr\equiv(O_2K)_3$$
$$|$$
$$O_2$$
$$|$$
$$O=Cr\equiv(O_2K)_3$$

, containing sexavalent chromium.

The addition of H_2O_2 to a soluble chromate gives the red compounds (I.) in the presence of alkali, and the blue compounds (II.) in acid solution. No reaction takes place in very strong alkaline solution, because the excess of alkali destroys the H_2O_2; the best results are obtained at a low temperature. When 30 per cent. H_2O_2 is added to an alkaline chromate solution at 0°, the liquid becomes almost black. On allowing to stand in the cold, reddish-yellow crystals of the alkali salt separate. It is slightly soluble in water, giving a brown solution which is stable in the presence of free alkali. The compounds are stable when dried. On moistening with strong sulphuric acid they are liable to explode violently like the blue perchromates. The free acid $H_3CrO_8,2H_2O$ is said to be produced as a crystalline substance at temperatures below $-30°$; as the colour is blue, it is assumed that the constitution does not correspond to that of the red salts.

The blue perchromates have a dark violet-blue colour with a red pleochroism. The very slightly soluble pyridine salt occurs as shining needles, which are easily dried and have the formula II. The work of Schwarz and Giese,[4] however, suggests that the blue compound is not an acid but a peroxide CrO_5, the pyridine and ammonia compounds being addition products. The potassium and ammonium salts are obtained in the form of almost black powders, of a constitution corresponding to type III. Free perchromic acid cannot be extracted with ether until aqueous solutions of these salts have been acidified. For example, when an aqueous solution of $K_2Cr_2O_7$ is treated with H_2O_2, the blue colour appears, but acid must be added before extraction is possible. This blue coloration is a very delicate test for either chromates or H_2O_2, and is visible in dilutions of 1 in 40,000. The only substances which mar the reaction are vanadic acid and, to a smaller extent, molybdic and tungstic acids. Schwarz and Giese[5] consider that $KCrO_5.H_2O_2$ should be formulated $KCrO_6.H_2O$, for there is not a quantitative relationship between loss of water and

[1] *Z. anorg. Chem.*, 1931, **204**, 67.

[2] Tjabbes, *Z. anorg. Chem.*, 1933, **210**, 385.

[3] *Ibid.*, 1932, **209**, 175.   [4] *Ber.*, 1932, **65**, 872.   [5] *Ber.*, 1933, **60** [B], 310.

oxygen in a tensimeter; the unstable thallous perchromate is probably $TlCrO_6$. The constitution assigned is

$$IIa. \quad \left(\begin{smallmatrix} O \\ | \\ O \end{smallmatrix}\right)_2 Cr(OK).O.O.(KO)Cr\left(\begin{smallmatrix} O \\ | \\ O \end{smallmatrix}\right)_2.$$
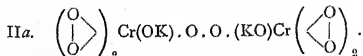
The perchromates are unstable in solution. The blue solutions are reduced to tervalent chromium salts in the presence of acid; the red solutions, in the presence of alkali, are reduced to chromates. The original compound is thus reproduced, so that the chromates act as catalytic agents for decomposing alkaline H_2O_2. The reaction is not, however, a perfect example of catalysis, as part of the chromate, even in alkaline solution, is reduced to the tervalent state.

The perchromic acids are not strong acids. The strongest is H_3CrO_8, and even this is weaker than acetic acid. The only salts known are those of the alkali metals and of organic bases.

A *chromium tetroxide*, CrO_4, exists in the form of double compounds; it shows no acidic properties. The probable constitution is $O_2Cr\left\langle\begin{smallmatrix} O \\ | \\ O \end{smallmatrix}\right.$,

and the oxide is therefore a derivative of sexavalent chromium. Addition products with 3 mols. of ammonia are precipitated as dark brown needles or plates, when a cold, ethereal solution of perchromic acid is mixed with strong ammonia. They dissolve in water to give a dark brown solution, are stable when dry, and volatile when warmed. The ammonia in these compounds is directly attached to the chromium, for chromammines are formed by the action of hydrochloric acid. Other interesting examples of addition compounds of CrO_4 include those with potassium cyanide:

$$\left[CrO_4(CN)_6\right]K_6 \qquad \left[(CrO_4)_2(CN)_6\right]K_6, 5H_2O \qquad \left[CrO_4\genfrac{}{}{0pt}{}{NH_3}{(CN)_2}\right]K_3, 5H_2O,$$
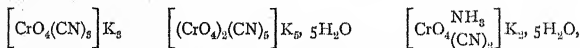
in which the potassium can be replaced by other metals; there is also an addition product with 1 mol. of hexamethylenetetramine, and another which contains 1 mol. of ethylenediamine and 2 mols. of water. All these compounds are brown.

The other Per-acids of the Metals.—The formation of the other per-acids by treatment with H_2O_2 is unaccompanied by any increase in the valency of the metal; the oxygen atom is simply replaced by the —O—O— group. It is not easy to determine which of the formulae $O_2VO.OH$ or $\begin{smallmatrix} O \\ | \\ O \end{smallmatrix}\rangle V\langle\begin{smallmatrix} OH \\ \\ O \end{smallmatrix}$ should be assigned to pervanadic acid; a
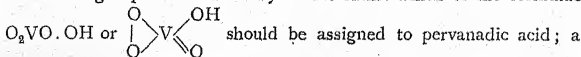
co-ordination formula such as $\left[V\genfrac{}{}{0pt}{}{O_2}{O.O}\right]H$ is really the same as the others. In solution, equilibria of the type $R.OH + H_2O_2 \rightleftharpoons R.OOH + H_2O$

exist. The percentage of per-acid present, when the state of equilibrium is attained, increases in passing from $V \longrightarrow Nb \longrightarrow Ta$. Hence the pertantalates are the most stable. They are decomposed by sulphuric acid only when heated, while the pervanadates are decomposed in the cold, with evolution of oxygen; pervanadic acid decomposes H_2O_2 catalytically. Polypertantalates of the formula $O_3Ta[O.OM]_3$ are also known, but niobium and vanadium do not give these compounds. These two metals, besides forming the acids HVO_4 and $HNbO_4$ (free HVO_4 only exists in solution), give so-called pyro-per-salts of the probable constitution $O : \left[VO_2 \diagup \begin{smallmatrix} OM \\ O.OM \end{smallmatrix} \right]_2$. The tendency to form per-acids also increases with rise in atomic weight in the metals belonging to the molybdenum-tungsten group.

Salts of the acid $O_2W(OH)(OOH)$ are readily produced by adding H_2O_2 to a boiling solution of a tungstate; when the reaction is carried out at a lower temperature, compounds still richer in oxygen can be obtained, e.g. $K_2WO_6 . H_2O$; the composition of the free acid, which has not been isolated from solution, varies between $O_2W(OH)(OOH)$ and $O_2W(OOH)_2$. Permolybdates, however, yield compounds of the type $xR_2O, yMoO_4$ only with difficulty on acidification, most of the products containing MoO_8. The caesium salt, $Cs_2O,4MoO_4$, is the richest in oxygen. The composition of the permolybdates depends upon the acidity of the solution; the per-salts also form series, like the ordinary molybdates, which are derived from isopolyacids, e.g. the para- series and the tetra- series, etc. These compounds are very numerous, and show the reactions of H_2O_2 owing to hydrolysis; they are at once destroyed by alkali with evolution of oxygen. Peroxidation proceeds further in acid solutions than with the solid salt. Distribution experiments prove that the acid H_2MoO_6 is formed in solution as well as H_2MoO_5. Per-compounds derived from polyacids of tungsten have not been prepared. Salts of the formulae $Na_2W_2O_8,2H_2O$, $Na_2W_2O_9,6H_2O$ and K_2WO_8,H_2O are known. Many poly-permolybdates and tungstates have been described.[1] Some are considered to be analogous to the perchromates (see p. 514), and are formulated $(O_2)_2 \equiv M = (O_2R)_2$, containing sexavalent Mo or W.

All these compounds are produced by the addition of H_2O_2 to a solution of the normal salt; those of the heavy metals can also be prepared by the double decomposition of the solution of the alkali per-salt. Many of them can only be prepared in the amorphous state. The alkali salts are very soluble, but can usually be precipitated with alcohol; the salts of the heavy metals can seldom be obtained pure, and are never well defined. The colours of the per-salts are very characteristic, and can sometimes be used as a test for the metal or for H_2O_2. The usual colour is yellow or orange (cf. pertitanic acid, p. 843).

[1] Rosenheim, Hakki and Krause, Z. anorg. Chem., 1932, 209, 175.

The pertantalates, however, give white powders. The pertungstates are only slightly coloured, but the yellow colours of the per-salts of vanadium, molybdenum and uranium are very characteristic. The free acids are themselves coloured, and hence acid solutions are yellow. The addition of H_2O_2 to an acidified molybdate solution gives a deep yellow liquid, from which the free acid can be isolated, but, like its chemical relatives, only in an amorphous condition. A few salts of voluminous cations (e.g. $Zn(NH_3)_4^{..}$) can be obtained.[1] When crystallised from alkaline solutions they are deep red and explosive, while the acids are yellow and more stable and probably have the

formula $M_2^I \begin{bmatrix} O_2 & O_2 \\ O_2 & O_3 \end{bmatrix}$ or $MO.O.\overset{O-O}{\underset{O-O}{\overset{\vee}{\wedge}}}Mo.O.O.M.$ Free pervanadic
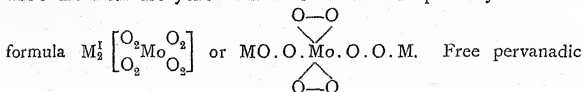
acid is the most unstable, and is decomposed on warming. It cannot be isolated as a solid, while pertantalic acid is obtained as a white powder ($HTaO_4$) when the potassium salt is decomposed with sulphuric acid. According to J. Meyer and A. Pawletta,[2] the characteristic red colour produced by the action of hydrogen peroxide on a sulphuric acid solution of vanadic acid is not free pervanadic acid but a peroxide sulphate, $(VO_2)_2(SO_4)_3$, containing quinquevalent vanadium in the cation. Dialysis of potassium perniobate, after acidifying with sulphuric acid, gives colloidal perniobic acid, which is left on evaporation as a yellow, insoluble coagulum. Similarly, pertungstic acid, which is produced by heating WO_3 with H_2O_2, will not crystallise from the resulting yellow solution. The behaviour of peruranic acid is peculiar. A yellow-white precipitate of the formula $O_2U(OH)(OOH)$, H_2O is thrown down when H_2O_2 is added to a uranyl salt. This precipitate dissolves in water to the extent of only 5-10 mg. per litre, but is extremely soluble in solutions of alkalis, from which orange-red salts of the composition M_2O_2,UO_4, aq., or $2M_2O_2,UO_4$, aq., can then be crystallised. These alkali compounds are very soluble in water.

Part of the oxygen in most of these per-acids can be replaced by fluorine; e.g. vanadium, niobium, tantalum and tungsten give these fluoro-per-acids.

[1] Gleu, Z. anorg. Chem., 1932, 204, 67.
[2] Z. physikal. Chem., 1927, 125, 49.

IV. THE COMPOUNDS OF SULPHUR, SELENIUM AND TELLURIUM

CHAPTER XIX

HYDROGEN COMPOUNDS OF SULPHUR, SELENIUM AND TELLURIUM

Hydrogen sulphide, selenide and telluride—Sulphides—Hardness—Thiosalts—Polysulphides

Hydrogen Sulphide, Hydrogen Selenide and Hydrogen Telluride

Preparation and Stability.—The most important methods of preparation are: (1) direct union of the elements; (2) hydrolysis of sulphides, selenides, etc.

Synthetic Preparation.—The heats of formation of the compounds H_2O, H_2S, H_2Se and H_2Te show a progressive diminution in this order. Most of the other properties of water, however, are essentially different from those of the remaining three compounds, *e.g.* the tendency to polymerise, the lack of acidity, absence of smell, etc. The heat of formation of water (liquid) is 68·9 Cals., that of H_2S much less (7·2 Cals. when formed as a gas by direct union of gaseous elements); H_2Se has a negative heat of formation at room temperature ($-2\cdot0$ Cals., using gaseous selenium), and H_2Te is strongly endothermic.

While oxygen and hydrogen can unite with explosive violence, the combination of sulphur and hydrogen proceeds quietly, and although the reaction is slow it is almost complete. The decomposition of sulphuretted hydrogen is perceptible only at high temperatures, and the compound is only split up entirely at 1690°. With selenuretted hydrogen a definite state of equilibrium is set up at about 100°, according to the equation $H_2 + Se \rightleftharpoons H_2Se$; while the proportion of H_2Te present in the corresponding equilibrium of hydrogen and tellurium is smaller than in that of H_2Se. The amount of hydrogen combined with the selenium or tellurium increases with rise of temperature, while H_2S becomes less stable as the temperature is raised. There appears to be a definite temperature at which the stability of H_2Se is at a maximum, the percentage decomposition increasing

both above and below this temperature. According to Pélabon,[1] the reactions between hydrogen and sulphur or selenium are examples of "false" equilibria, *i.e.* direct combination of the elements does not give equilibrium mixtures of the same composition as those which result from decomposition of the compounds carried out at corresponding temperatures. Bodländer, however, has shown that the same equilibria are produced by direct union, but extremely slowly.[2] Similarly, the rate of reaction between oxygen and hydrogen falls off rapidly at temperatures below the explosion point. The reaction of hydrogen with sulphur and with selenium is affected by temperature in the same way. The presence of solid selenium on the walls of the vessel also has an important influence on the latter reaction. The amount of combination is found to be proportional to the surface of the selenium; other conditions being equal, the rate of the reaction is almost entirely determined by the exposed surface of the element (*cf.* p. 392). This factor may be related to the property of occluding H_2Se which is possessed by molten selenium; on cooling, the gas is expelled.

Hence the displacement of the equilibrium $H_2 + S \rightleftharpoons H_2S$ with rise of temperature favours the production of the free elements, while the equilibria $H_2 + Se(Te) \rightleftharpoons H_2Se(H_2Te)$ are affected in the opposite sense. Thus the quantities of H_2Se in equilibrium mixtures are:—

Temperature			254°	301°	356°	405°	493°
Per cent. H_2Se			13.9	20.5	25.9	30.5	37.7

At room temperature the rate of decomposition of hydrogen selenide is very slow, but hydrogen telluride is unstable even below 0°; and the aqueous solution gradually decomposes.

The synthesis of sulphuretted hydrogen involves three processes. First, an extremely rapid breakdown of complex S_x molecules into diatomic molecules, followed by an equally quick change $S_2 \longrightarrow 2S$, and, finally, the actual combination of the elements. Obviously the experimental results will give the velocity of the third process only, viz. $H_2 + S = H_2S$.

These hydrides are also formed by the action of nascent hydrogen upon sulphur, selenium and tellurium (*e.g.* zinc and an acid suspension of sulphur). The electrolytic method in which the negative element is used as cathode, gives good results only with tellurium, as this element readily dissolves to give Te'' ions. Unstable endothermic hydrogen compounds can be used instead of nascent hydrogen; for example, H_2S or H_2Se is obtained by the action of hydrogen iodide on sulphur or selenium. These reactions, however, are reversible (*cf.* pp. 169, 218). The formation of a little H_2S when steam is mixed with sulphur vapour is due to the slight decomposition of steam at high temperatures.

[1] Pélabon, *Z. physikal. Chem.*, 1899, 26, 657.
[2] Bodländer, *Z. physikal. Chem.*, 1899, 29, 315, 429.

Preparation by Hydrolysis.—This general method of preparation consists in hydrolysing sulphides, selenides and tellurides. Hydrolysis is started by the action of water on the sulphide, etc., but the process must usually be assisted by adding acid. The sulphides of aluminium and boron, and some of the sulphides of phosphorus, are completely decomposed by water alone, and sulphuretted hydrogen is evolved in a steady stream. The corresponding compounds of selenium and tellurium give analogous reactions.

When water acts upon the sulphides of the alkali and the alkaline earth metals the gas remains in solution. The reversible reaction $Na_2S + 2H_2O \rightleftharpoons 2NaOH + H_2S$ is in a state of equilibrium when only a small quantity of sulphuretted hydrogen is present and the solubility product of the H_2S is not reached. H_2S can be expelled by heating the solution, without adding any acid, especially when the hydrosulphide is employed. A steady stream of H_2S is obtained when an aqueous solution of $Mg(SH)_2$ is warmed. Acid must be added when an insoluble sulphide is used, because the S'' or SH' ions are then reprecipitated almost at once as metallic sulphides, and the quantity of H_2S formed in solution is quite inappreciable. Sulphuretted hydrogen is usually prepared by treating artificial iron sulphide with dilute sulphuric or hydrochloric acid in a Kipp's apparatus. The uncombined iron in the sulphide increases the vigour of the reaction with acid. Although water does not react with iron sulphide, H_2S is produced by passing steam over red-hot iron sulphide according to the equation $FeS + H_2O \longrightarrow FeO + H_2S$. H_2S prepared from iron sulphide may contain hydrogen, hydrocarbons and arsine, owing to presence of impurities in the raw materials. Arsine can be removed by passing the gas over red-hot alkali polysulphides, which form thioarsenites, or by treating with iodine in the cold. Pure sulphuretted hydrogen is obtained by the action of acid on precipitated sulphides. A gas free from hydrogen and arsine is conveniently prepared from barium or calcium sulphide. These sulphides are made by the reduction of the sulphates with charcoal at a red heat; technically the decomposition is brought about by low-pressure steam. When these sulphides are used in Kipp's apparatus they are mixed with a little burnt gypsum, moistened with water and compressed into cubes.

Large quantities of sulphuretted hydrogen or selenuretted hydrogen are rapidly produced when organic compounds rich in hydrogen, such as paraffins, naphthalenes and resins, are heated with sulphur (or selenium). Sulphuretted hydrogen is formed during the decay of organic sulphur compounds, and also as a result of certain bacterial processes. The gas is produced by reducing oxygen compounds of sulphur, *e.g.* by the action of hydriodic acid on concentrated sulphuric acid.

Properties.—H_2S and H_2Se are colourless in the liquid and solid

states, but H_2Te gives a greenish-yellow liquid and crystallises in
the form of lemon-yellow needles; thus increase in atomic weight is
accompanied by the development of colour.   In this respect the sulphur
group of elements resembles the halogens.   The following table gives
melting and boiling points and densities in the liquid state:

	H_2S	H_2Se	H_2Te
Melting point .	$-82 \cdot 9°$	$-64°$	$-54°$
Boiling point .	$-60 \cdot 1°$	$-42°$	$-1 \cdot 8°$
Density (at b.pt.) .	$0 \cdot 96$	$2 \cdot 12$	$2 \cdot 6$

Unlike water, which expands on freezing, the solids have a higher density than
the liquids; water is also unique in having relatively high melting and boiling
points.   Molecular polymerisation is the cause of the high density of water (cf. p. 399).

The characteristic smell of sulphuretted hydrogen, observed during
the putrefaction of eggs, is more intense than that of H_2Se or H_2Te,
which resembles arsine in smell.   The odour of H_2Se is somewhat
like H_2S, but it has a pungency not possessed by the sulphur
derivative.   Small quantities of H_2S do not irritate the mucous
membrane; but work with H_2Se, in spite of its weaker smell, soon
becomes unpleasant, causing catarrh and inflammation of the eyes.
Sulphuretted hydrogen is extremely poisonous, especially when inhaled,
but less so when absorbed through the skin.

The gases are fairly soluble in water.   The solubility of H_2S per
unit vol. of water is:

Temperature .	$0°$	$10°$	$20°$	$30°$	$40°$
Vols. H_2S .	$4 \cdot 4$	$3 \cdot 6$	$2 \cdot 9$	$2 \cdot 3$	$1 \cdot 9$

The solubility of H_2Se is almost the same: viz. $3 \cdot 8$ vols. dissolve at
$4°$ and $2 \cdot 7$ vols. at $22 \cdot 5°$.   The figures for H_2Te are uncertain, as the
solution is very unstable. H_2S is more soluble in alcohol than in water,
e.g. $17 \cdot 9$ vols. dissolve at $0°$.   When saturated aqueous solutions of H_2S
and H_2Se are cooled, crystalline fairly stable hydrates separate, which are
comparable with chlorine hydrate.   The sulphur compound probably
has the composition $H_2S, 6H_2O$ and exerts a vapour pressure of 1 atmos-
phere below $0 \cdot 4°$; H_2Se aq. exerts a pressure equal to 718 mm. of H_2Se
at $7 \cdot 5°$.   These compounds are stable at higher temperatures under
increased pressure, e.g. the hydrate of H_2S can be heated to $28 \cdot 5°$ under
a pressure of 16 atmospheres, but decomposes above $29°$, no matter
how much the pressure is increased. H_2Se, aq. does not exist above $30°$.

The liquefied gases, in contrast to water, are poor solvents for salts.
Aluminium halides are soluble in liquid hydrogen sulphide, and a few
halides of other metals (e.g. $ZnCl_2$, $FeCl_3$, $HgCl_2$). PCl_3, $SiCl_4$ and SO_2
also dissolve without forming compounds with the hydrogen sulphide.
Hydrogen chloride and hydrogen bromide dissolve easily, but the
solutions are not acidic and do not conduct electricity.   The solvents

themselves are neutral except when greatly diluted with water. These dilute solutions redden litmus, but the colour fades as the water evaporates. They are very weak acids, and even carbon dioxide decomposes alkali sulphides. Conductivity measurements with a solution of H_2S indicate that ionisation is arrested at the SH' stage.

The chemical properties of the gases are dependent upon either their reducing power or their acid nature. Many of the metallic salts are characteristic. As would be expected, hydrogen telluride is the strongest, and hydrogen sulphide the weakest, reducing agent, for the former, owing to its strongly endothermic character, decomposes spontaneously even in the dark, while hydrogen sulphide is stable except in the presence of oxidising agents. The gases are oxidised by the air in presence of moisture, but the perfectly dry gases are unaffected. A solution of H_2S contained in a loosely stoppered bottle deposits white sulphur: $H_2S + O \longrightarrow H_2O + S$. The decomposition of H_2Se is more rapid; a red coloration appears first, and eventually red flakes of selenium are deposited. The solution stains the skin brownish red, and the colour adheres very firmly. The oxidation of H_2S by excess of oxygen gives sulphur dioxide; actually sulphur is the initial product, but when the temperature rises above its ignition point the element burns to the dioxide: $H_2S + O \longrightarrow H_2O + S$ or $H_2S + 3O \longrightarrow H_2O + SO_2$; the free sulphur is thus recovered in industrial processes (Chance). Hydrogen sulphide burns in the air with a pale blue flame, but when a mixture of it with oxygen is ignited an explosion takes place. The products of the combustion of telluretted hydrogen are analogous to those of H_2S, but the flame is more luminous. Similar reactions occur with liquid oxidising agents such as chlorine and bromine water. Sulphur is sometimes deposited, but if an excess of halogen is present further oxidation to sulphuric acid takes place; sulphur halides are formed as intermediate products. Nitric oxide and fuming nitric acid react vigorously with sulphuretted hydrogen; if a drop of fuming nitric acid is added to a vessel filled with the gas an explosion occurs. Concentrated sulphuric acid can oxidise hydrogen sulphide to sulphur and sulphur dioxide to such an extent, even in the cold, that concentrated sulphuric acid must not be used to dry the gas. Sulphides are also oxidised by H_2O_2 to thiosulphates and finally to sulphates. The powerful solvent action of fuming nitric acid or free halogens is used to dissolve insoluble sulphides.

The slight analogy between H_2S and H_2O is further indicated by the difficulty in making addition compounds with hydrogen sulphide. A few metal halides, such as those of aluminium and some, but not all, of those of beryllium, titanium and quadrivalent tin, form addition compounds containing 1, 2 or 4 molecules of H_2S. The most stable of

these compounds is $AlBr_3 \cdot H_2S$, which decomposes at 30°, though most of the others are not stable above −40°. Again, thiohydrolysis, corresponding to hydrolysis, seldom occurs; but the halides of phosphorus, arsenic, antimony and sulphur are decomposed by H_2S with evolution of halogen acids.

Sulphides, Selenides and Tellurides

The chemical nature of these salts is mainly due to the weakness of the parent acids; some of the salts have characteristic colours and are insoluble. Owing to these properties the metallic sulphides are of great value in qualitative analysis. The following description of the sulphides applies throughout to the selenides and tellurides, except where otherwise stated.

Both the hydrogen atoms in sulphuretted hydrogen can be replaced by metals, and so two series of salts exist: the normal sulphides of the type M_2S and the acid sulphides of the formula MSH. Telluretted hydrogen gives only normal salts. The acid selenides and sulphides are confined to those of alkali and alkaline earth metals and magnesium. The acid or hydro-sulphides are prepared by using excess of sulphuretted hydrogen and the normal salts by using theoretical quantities of acid and base. The acid salts of the alkali metals are made by saturating a solution of the alkali hydroxide with sulphuretted hydrogen: $MOH + H_2S \longrightarrow MSH + H_2O$; in order to obtain the normal sulphide the hydroxide solution is divided into two parts. The first portion is saturated with H_2S, which gives MSH, and then the second portion is added. The following reaction occurs: $MSH + MOH = M_2S + H_2O$.

Many of the sulphides, selenides and tellurides, especially those with large heats of formation (cf. p. 441), are obtained by grinding together the metal and non-metal. The reaction with sodium and potassium is explosive, and mercury, iron, magnesium and even copper combine directly when in a very finely divided condition. Other metals such as lead or nickel require to be heated, and in some instances a very high temperature is necessary to start the reaction; e.g. aluminium can be strongly heated in sulphur vapour without much effect, but if the intense heat of burning magnesium ribbon is concentrated upon a small area of a solid mixture, a reaction is started which spreads throughout the entire mass. Aluminium telluride, used for the preparation of hydrogen telluride, is produced when the elements are ground together. Heavy metal sulphides can be employed instead of free sulphur, e.g. aluminium sulphide is obtained by fusion of the metal with the sulphides of zinc, lead or antimony. The formation of K_2Te by the electrolysis of aqueous KOH, using a tellurium cathode, is also based upon the same principle. Potassium is liberated at the cathode and at once attacks the tellurium.

An important method of preparation of sulphides, selenides and tellurides, especially those of alkali and alkaline earth metals, consists in the reduction of oxidised compounds. The sulphates are generally used, although, of course, sulphites and thiosulphates are equally suitable; carbon, or sometimes carbon monoxide or hydrogen, acts as reducing agent. With carbon, the reaction is represented by the equation

$$M_2SO_4 + 2C \longrightarrow M_2S + 2CO_2.$$
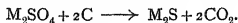
This process is applied to the industrial preparation of the sulphides, for coal is a cheap reducing agent, while the sulphates of the alkali and alkaline earth metals are met with in large quantities, both in nature and as by-products of chemical industry. Formerly the recovery of sulphur in the Leblanc soda process depended upon this action (*cf.* p. 809). Selenates and tellurates are reduced more easily than sulphates; *e.g.* BaSe is readily prepared by reduction of $BaSeO_4$ with hydrogen.

A pure sulphide is obtained when the oxide of a heavy metal is heated with sulphur. With metals of the alkali and alkaline earth groups, however, only part of the oxygen is replaced, and thiosulphates are produced; also, the excess of sulphur combines with the sulphide to give polysulphides. This reaction also takes place with hydroxides and carbonates—the latter give off carbon dioxide during the process. If an alkali carbonate is fused with sulphur a complex mixture is formed, which is termed "liver of sulphur" on account of its brown colour. The mixture contains sulphide, polysulphide, carbonate, thiosulphate, and sulphate. If metallic oxides are heated to redness in sulphuretted hydrogen or carbon disulphide vapour, pure sulphides are obtained.

Heavy metal sulphides, which are all insoluble in water, are prepared by the well-known method of passing hydrogen sulphide through solutions of salts. As the sulphides are exceptionally insoluble, it is unnecessary to start with soluble salts, for sulphuretted hydrogen attacks a suspension of an insoluble compound in water. This method may be utilised for the conversion of the chlorides of mercury, silver and lead into sulphides, provided the solution is not too acid. Metallic sulphides which are soluble in acids are not precipitated by sulphuretted hydrogen, owing to the production of free acid by double decomposition: $MCl_2 + H_2S \rightleftharpoons MS + 2HCl$. The liberation of free acid is prevented by using ammonium sulphide in place of hydrogen sulphide, and the sulphide is then precipitated: $MCl_2 + (NH_4)_2S \longrightarrow MS + 2NH_4Cl$ (*cf.* p. 533). A better method of obtaining some sulphides is to acidify solutions of the sulpho-salts (pp. 537-539). MoS_3, V_2S_5 and WS_3 may be prepared in this way.

Properties.—The properties of the alkali and alkaline earth sulphides and those of magnesium and the earth-forming metals, aluminium and chromium, differ considerably from the sulphides of the remaining

metals. The alkali and alkaline earth sulphides (also selenides and tellurides) are soluble in water and can be crystallised from solution. The sulphides of chromium and aluminium probably dissolve momentarily, but are quickly hydrolysed with the precipitation of insoluble hydroxides. The sulphides of the heavy metals are very insoluble, and on this account it is difficult to determine the extent of hydrolysis, but it may be assumed that any portion of the sulphide which does dissolve is completely hydrolysed. They are either anhydrous or contain merely adsorbed water when in the colloidal state. Sulphides of the first class are white; those of the second class are all coloured, except zinc and germanium sulphides.

The sulphides of the rare earths prepared in the dry way are coloured, *e.g.* :—

Metal	Ce^{III}	La and Y	Pr	Nd
Colour of sulphide	Red-black	Yellow	Brown (?)	Olive

Normal praseodymium sulphide, Pr_2S_3, is remarkable inasmuch as it can be made only in the presence of considerable quantities of cerium, which affects the colour. In its absence there is a great tendency to form the yellow oxysulphide, PrSO.

Sulphides of the first class often appear coloured, when prepared in the dry way, *e.g.* alkali sulphides produced by drying the hydrated forms have a reddish tint, and selenides of the alkaline earths are rose coloured; also, when H_2Te is passed through caustic soda the liquid turns red. These colours, however, are due to decomposition. Free sulphur, selenium or tellurium are formed by oxidation, and these combine with the undecomposed salt to give coloured polysulphides, etc. A colourless liquid, which deposits colourless crystals, can be obtained from H_2Te and alkali hydroxide, if full precautions are taken to prevent oxidation. A similar result is obtained by using H_2S or H_2Se. When these solutions are allowed to stand in the air, hydrolysis takes place, giving free H_2S, H_2Se or H_2Te, which are then oxidised to the free elements, and the solutions become coloured. The sulphide solutions turn yellow, those of selenium brown, and those of tellurium a deep red. The pink colour of the alkaline earth and zinc selenides is due to free selenium. Heavy metal selenides are mostly brown or black. Fused tellurides of the heavy metals have a bright metallic lustre; synthetic aluminium telluride is described as a black, metallic sintered mass.

When freshly precipitated, the sulphides of the heavy metals are often colloidal, but it is possible to convert them into the crystalline form. CuS and CdS are said to become crystalline almost at once after being thrown down; other sulphides slowly assume the crystalline state when kept at a temperature of 300°, some only after prolonged heating with a solution of ammonium sulphide. All sulphides, including those of the alkali metals prepared in the dry way, can be obtained in the crystalline form if the fused compounds are allowed to solidify; the alkali sulphides crystallise in cubes. The alkaline earth compounds have to be heated to the temperature of the electric furnace before fusion occurs. Al_2S_3 is very difficult to melt. Heavy metal sulphides, when crystalline, often have a metallic lustre, and are good conductors of electricity, but are distinguished from metals by their brittleness.

The hydrolysis of sulphides is of great importance in chemistry. The sulphides of the metals of the earths are immediately hydrolysed

by water with evolution of H_2S. These sulphides smell of H_2S in damp air.[1] The derivatives of the heavy metals are hydrolysed if heated in a current of superheated steam. The alkali and alkaline earth sulphides are only partially hydrolysed in solution; the chief product is the hydrosulphide: $M_2S + H_2O \rightleftharpoons MSH + MOH$. Na_2S hydrolyses almost entirely in this manner in dilute aqueous solution; the degree of hydrolysis of a $N/10$ solution is at least 86·4 per cent.; on the other hand, a solution of NaSH at 25° is hydrolysed only to the extent of 0·12 per cent. The solutions of the alkali metal sulphides therefore have a strongly alkaline reaction. The normal sulphides of the alkaline earths and magnesium are almost completely decomposed by water (except BaS, $6H_2O$, which crystallises in thin plates), owing to the comparative insolubility of the hydroxides. Thus half the metal present is converted to the hydrosulphide, and half to the hydroxide: $2CaS + 2H_2O \longrightarrow Ca(SH)_2 + Ca(OH)_2$. Crystalline $Ca(SH)_2$ is prepared by forcing H_2S through a thick milk of lime, keeping the liquid cold. The lime quickly dissolves and, on standing, colourless prisms of $Ca(SH)_2$, $6H_2O$ separate out. Normal magnesium sulphide cannot be obtained from aqueous solutions, but precipitated $Mg(OH)_2$ readily dissolves in excess of sulphuretted hydrogen, forming $Mg(SH)_2$. When the solution is warmed H_2S is evolved and $Mg(OH)_2$ again thrown down. Solutions of sulphides generally lose H_2S when warmed, and prolonged boiling causes complete decomposition.

Alkali sulphides dissolve readily in alcohol as well as in water; even $Ca(SH)_2$ is soluble in alcohol; 100 g. of an aqueous solution of Na_2S contain 13·4 g. Na_2S at 10° and 24·2 g. at 45°. The alkali sulphides are hygroscopic, but concentrated solutions deposit well-defined crystals which usually contain much water. The common hydrate of sodium sulphide is Na_2S, $9H_2O$; above 48·9° it loses water, forming lower hydrates, of which those with 6, 5·5, 5 and 4·5 mols. have been described. K_2S crystallises with 12, 5 or $2H_2O$, Rb_2S with $4H_2O$. Sodium selenide gives hydrates with 4, 5, 9, 10 and 16 mols. H_2O. The acid sulphides combine with smaller quantities of water, and KSH contains only $\frac{1}{2}$ mol. H_2O. Ammonium sulphide cannot be prepared in the solid state from aqueous solutions because it dissociates very readily into NH_3 and H_2S, but is obtained as a colourless crystalline compound from a mixture of the two gases kept at about $-18°$. At higher temperatures it decomposes thus: $(NH_4)_2S \longrightarrow NH_4HS + NH_3$. Consequently, unless the mixed gases are kept cold, colourless needles of $(NH_4)SH$ only are produced. At atmospheric pressure no combination occurs above 32·5°, for at this temperature the

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[1] The sulphides of cerium and lanthanum made by the fusion method are attacked only by boiling water, but those of praseodymium, neodymium and yttrium are decomposed more easily.

total pressure of the NH_3 and H_2S is 760 mm. This dissociation pressure is as follows:

Temperature	.	.	$4 \cdot 2°$	$22°$	$32 \cdot 6°$	$44 \cdot 4°$
Mm. .	.	.	132	410	772	1560

$(NH_4)_2Se$ and NH_4SeH seem to be rather more stable than the sulphur compounds.

In common with many ammonium salts, $(NH_4)_2S$ possesses the property of absorbing ammonia gas at very low temperatures. If a mixture of NH_3 and H_2S containing excess of the former gas is led through a tube in a freezing mixture of salt and ice, a heavy, oily, yellow liquid is produced, having approximately the composition $(NH_4)_2S, 2NH_3$. It decomposes when warmed.

Hydrazine sulphide, N_2H_4,H_2S, is about as stable as NH_4HS. While the normal sulphide is produced only at very low temperatures, the hydrosulphide is produced in the form of long hygroscopic crystals, very similar to sulphuric acid chamber crystals, by treating perfectly dry hydrazine with H_2S; it has a dissociation pressure of 86 mm. at 17° and 240 mm. at 29°.

Heavy Metal Sulphides. — *Appearance.* — The sulphides of the heavy metals usually have a characteristic appearance (for those of arsenic and antimony see above p. 739). Many of them occur in nature as metallic-looking minerals; *e.g.* silvery galena (PbS), brassy iron pyrites (FeS_2) and millerite (NiS), yellow greenockite (CdS), the leaden-grey molybdenum glance (MoS_2), which is very like graphite in appearance, bismuth glance (Bi_2S_3), copper glance (Cu_2S), also the nearly lead-black argentite Ag_2S, the black manganese glance MnS, etc. A few are more brightly coloured and have no metallic lustre, for example crimson cinnabar (HgS), white zinc blende (ZnS), and the indigo-blue copper mineral covelline (CuS). The sulphides of heavy metals often possess a metallic lustre when prepared in the dry way, either by fusion of the metal with sulphur or by reduction processes at high temperatures; most of them appear black or grey, and resemble graphite, while a few possess brighter colours.

Thus SnS and Bi_2S_3 prepared artificially by these methods have a leaden-grey appearance, Mo_2S_3 and US_2 are more like steel or iron in colour, PtS and WS_2 are nearly black, as also GeS, which, however, is red and transparent in thin layers. Ga_2S_3 and GaS are yellow, and Ga_2S is greyish-black. CrS is black, while Cu_2S has a black colour with a blue sheen, and V_2S_3 is black with a bronze lustre; V_2S_3 and Cr_2S_3 resemble graphite; the latter, when heated less strongly, appears green. PdS and RhS have a perfectly metallic appearance, forming bluish-white reguline masses, and Pd_2S also has a high metallic lustre. Besides the sulphides HgS, CdS and ZnS already described, those of antimony and arsenic and the artificially prepared MnS have brighter colours. MnS has a vivid green tint, which becomes almost black when strongly heated. ThS_2 has a dark brown colour; the sulphides of iron, FeS, Fe_2S_3 and FeS_2, also have lighter colours: the latter is yellow with a

metallic lustre ; SnS_2 forms beautiful golden-yellow leaflets, known as mosaic gold. Finally, MnS_2 is an amorphous, brick red compound, and occurs naturally as the brown mineral hauerite.

Sulphides prepared from solutions of metallic salts by precipitation with hydrogen sulphide or alkali sulphides sometimes possess a lighter colour than when made in the dry way. This is because the precipitated compounds are more finely divided. The following list gives the colours of precipitated sulphides :

Ag, Tl^I, Au^{III}, Fe, Ni, Co, Cu^I, Cu^{II}, Hg^{II}, Pb^{II}, Pd^{II}, Rh^{III}	Black.
Sn^{II}, Bi, Mo^V, Mo^{VI}, V^V, W^{VI}, Pt^{IV}, Ir^{III}, Ir^{IV}, Au^I	Brownish black.
Os^{IV}, UO_2^{II}, Mo^{IV}, Ge^{II}	Yellowish brown to reddish brown.
Cd, As^{III}, As^V, Sn^{IV}, In^{III}	Yellow.
Sb^{III}, Sb^V	Orange.
Zn, Ge^{IV}	White.
Mn^{II} (see p. 530)	Flesh coloured or green.

Precipitated lead and nickel sulphides often have a silvery metallic skin. Black sulphides appear slightly coloured when very finely divided ; CuS has a greenish-black and nickel sulphide a brownish-black colour. The colours of sulphides are intense, and many of them are the basis of colouring matters which have a strong attraction for fabrics. White ZnS mixed with $BaSO_4$ (lithopone) is extensively used in paints ; cadmiopones are co-precipitated mixtures of cadmium sulphide and selenide and barium sulphate.

Selenides and tellurides are darker and more metallic in appearance than the sulphides. When precipitated from solution they are mostly dark brown or black ; when dry, nearly all of them are black ; even zinc selenide gives dark red crystals when prepared in the dry way, while that of cadmium is red to black. Precipitated $SnSe_2$ is dark orange, but when fused it becomes white and metallic ; Bi_2Se_3 also has a silver-white colour. The tellurides are even more metallic in appearance (an exception is CdTe, which is a translucent red compound), and their formulae are often similar to those of alloys, e.g. a copper telluride is known, having the formula Cu_4Te_3. These compounds are examined by the physico-chemical methods used for true alloys (cf. p. 865).

Isomeric Modifications.—Certain sulphides exist in different forms. The best known example is that of mercury sulphide, HgS, which is black when precipitated from solution, but occurs in nature as red cinnabar. The black variety is the less stable, and can be changed into the red form, but the reverse change is not possible at ordinary temperatures. The natural black mercuric sulphide (metacinnabar) gives the same radiogram as the black precipitated product. When heated, cinnabar becomes much darker, even black, but the red colour returns on cooling ; this phenomenon is one of the many instances of compounds darkening in colour when heated (cf. pp. 449, 464) ; if,

however, cinnabar is heated above 410° it remains black on cooling. The labile character of the black form is shown by the fact that it is always the first one to be produced in a reaction; according to Ostwald's rule, the more active, and therefore more labile form, is produced first. Thus the black HgS is obtained not only by precipitation with sulphuretted hydrogen, but also when a mixture of sulphur and mercury is heated. It becomes red when vigorously rubbed; cinnabar is, however, better prepared by heating the black variety with a solution of alkali sulphide till it dissolves; on crystallising, the stable form separates. Cinnabar is also formed when a mixture of sulphur with mercury or mercurial compounds is sublimed, as the velocity of the change, black $\longrightarrow$ red, is then much greater. For a description of black and red antimony sulphide see p. 740. Manganese sulphide also exists in two isomeric forms with different colours. It is precipitated as a flesh-pink substance, but can also be obtained in a greenish form. The latter variety is more stable. It is produced by prolonged heating of the pink form with excess of $(NH_4)_2S$ solution, and is also formed in the presence of certain salts. Green manganous sulphide always results from preparations in the dry way, and is crystalline, while the pink form is amorphous.

The sulphides of nickel and cobalt occur in different modifications. As is well known, these compounds are not precipitated from acid solutions, but when obtained in a non-acidic medium they at once undergo alteration, and pass into forms that are almost insoluble in dilute acids. Middleton and Ward[1] showed that the sulphides produced from nickel, bi- and ter-valent cobalt compounds in absence of air are $Ni(SH)_2$, $Co(SH)_2$ and $Co(SH)_3$, for on drying in nitrogen NiS, CoS and Co_2S_3 are obtained; the freshly prepared sulphides dissolve in acid with evolution of hydrogen sulphide, but show an "ageing" effect, becoming less soluble after keeping. In presence of air, the sulphides always contain oxygen, added initially at the sulphur atoms; the primary process thus leads, for example, to: $Ni\left(-S\diagup^{O}_{\diagdown H}\right)_2$, $Co\left(-S\diagup^{O}_{\diagdown H}\right)_3$, etc. Further addition of oxygen takes place at the sulphur atom, sulphate finally being formed; this is indeed the manner in which these sulphides dissolve, hydrogen sulphide not being evolved. Other sulphides can be converted to insoluble forms when dried and heated. Thus ignited zinc sulphide (Sidot's blende) is almost insoluble in acids. IrS, when first precipitated, dissolves readily in acids, but after it has been heated to redness is quite insoluble even in *aqua regia*. Cr_2S_3 is not precipitated by $(NH_4)_2S$ from chromic salts on account of its hydrolysis into $Cr(OH)_3$, but when prepared in the dry way and strongly ignited is also insoluble in acids. This behaviour of the

[1] *J. Chem. Soc.*, 1935, 1459.

sulphides is similar to that of metallic oxides, the chemical activity of which is much reduced after strong ignition (*cf.* p. 450). Precipitated ferric sulphide, Fe_2S_3, which is stable only in presence of free alkali, is transformed on standing into the isomeric $FeS.FeS_2$. Uranyl sulphide, which is only partially thrown down by ammonium sulphide, is chemically changed when warmed with a small excess of this reagent. The original brown amorphous precipitate becomes an olive-green crystalline substance which consists of a mixture of UO_2 and sulphur, and is of use in the quantitative estimation of uranium, as it is readily converted by heat into U_3O_8. The temperature of precipitation also has a considerable effect on the properties of the heavy metal sulphides. Nickel sulphide, precipitated hot, gives on oxidation in air a little free sulphur but mainly thiosulphate, while when thrown down from a cold solution sulphur is the main product and little thiosulphate is formed on oxidation.

Differences in the size of the component particles, without any change in the orientation of the atoms, are sufficient to cause alterations in the colours of sulphides. PtS_2 when freshly precipitated is dark brown, but on drying becomes black; the ordinary yellow cadmium sulphide becomes orange or red when the size of the grains is increased by digestion or precipitation in hot solutions. Physical changes which are not accompanied by alteration of colour are often detected by examining the crystalline structure. Zinc sulphide is an example of this dimorphism; in nature it crystallises in the cubic system as zinc blende, and in the hexagonal system as wurtzite. The latter is produced from the blende by heating to a high temperature, by sublimation in an atmosphere of hydrogen, hydrogen sulphide, sulphur dioxide, sulphur or nitrogen, and also by ignition at a white heat. MnS and ZnSe are iso-dimorphous with ZnS. CdS,[1] CdSe and CdTe can be obtained in both the cubic and hexagonal forms. CuS and Ag_2S occur both in the rhombic and cubic systems, and their transition points are $103°$ and $179°$ respectively.

Crystal Structure.—The arrangement of the atoms in the crystalline sulphides has been determined by the X-ray method, and is found to be very similar to that in the halides. The structure of calcium sulphide and the selenides of calcium, strontium and barium is a cubic face-centred lattice (p. 299) in which metal and sulphur atoms are arranged alternately. Lead sulphide and probably also manganese sulphide have a body-centred cubic lattice (p. 239). The structure of zinc blende and of greenockite, CdS, is more complex, and corresponds to that of the cuprous halides or of diamond (p. 883). The zinc atoms occupy the corners of the cube, and the corners of the inscribed tetrahedron are occupied by the sulphur atoms. Another form of zinc sulphide, wurtzite, has a structure different from that of

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[1] Milligan, *J. Phys. Chem.*, 1934, 38, 797.

zinc blende which is figured on p. 884. The crystal structures of pyrites, FeS_2, hauerite, MnS_2, CoS_2, MoS_2, WS_2, RuS_2, cobaltine, CoAsS, and ullmannite, NiSbS, are all alike. It can be shown that the sulphur atoms in pyrites lie close together in pairs at some distance from the atoms of iron. The latter form the usual face-centred cubic lattice, like metallic copper (Fig. 15, p. 19), and the bond between two sulphur atoms cuts that between two iron atoms in an oblique direction. Each iron atom is surrounded by six sulphur atoms arranged at the corners of an octahedron and belonging to six different S_2 groups. Conversely, each S_2 group is surrounded by six Fe atoms arranged octahedrally. In CoAsS and NiSbS a similar configuration is found, the S_2 groups of the pyrites being replaced by AsS and SbS respectively. They thus belong to the same type as solid CO_2 and N_2O.

Hardness of Sulphides and Hardness in General.—The sulphides, selenides and tellurides of the heavy metals are valuable material for the elucidation of the question of the origin of hardness of crystalline substances. Goldschmidt[1] has shown that the hardness of substances of the same empirical formula diminishes with increasing distance of the particles in the crystal and increases with the valency of the particles. The hardness arises from the electrostatic attraction of the particles and is therefore increased by the existence of many points of attraction and by the closeness of the charged particles to one another, since the electrical conditions are subject to the usual Coulomb law. The diminution of hardness with increase in the distance between the atoms is shown in the following list of compounds of bivalent metals :—

Distance between particles:	BeS	BeSe	ZnS	BeTe	ZnSe	CdS	HgS	CdSe	HgSe	ZnTe	HgTe	CdTe
	2·10	2·22	2·35	2·43	2·48	2·52	2·53	2·63	2·63	2·64	2·79	2·80 cm^{-8}
Hardness:	7·5	5·5	4	3·8	3—4	3·2	3	3·0	2·8	3·0	2·6	2·8

This relation holds whether the substances form atomic or ionic lattices and is independent of the nature of the union—polar or non-polar. In the next series of results the rise of hardness with increasing valency is obvious and the hardest of these compounds, MX, are those which contain bivalent elements when the distance between the particles is approximately the same in the pairs of substances :—

Distance between particles:	LiF	MgO	NaF	CaO	LiCl	SrO	NaCl	BaO	LiCl	MgS	
	2·02	2·10	2·31	2·40	2·57	2·57	2·81	2·77	2·57	2·59 cm^{-8}	
Hardness:	3·3	6·5	3·2	4·5	3·0	3·5	2·5	3·3	3·0	4·7	
Distance between particles:	NaCl	CaS	LiBr	MgSe	NaBr	CaSe	CaCl	CaTe	KI	BaTe	
	2·81	2·84	2·75	2·73	2·98	2·96	3·14	3·17	3·53	3·49 cm^{-8}	
Hardness:	2·5	4·0	2·5	3·5	2·4	3·2	2·3	2·9	2·2	2·6	

The rule thus extends to all kinds of atoms.

[1] *Geochem. Verteilungsgesetze*, viii., Oslo, 1926.

The following table shows the increase in hardness when with almost constant distance between the particles the valency varies from 1 to 4:

Distance between particles:	NaF	MgO	ScN	TiC
	2·31	2·10	2·23	2·23 cm $^{-8}$
Hardness:	3·2	6·5	7-8	8-9

It is easy to see that a desired degree of hardness can be attained by compensating an increase in the space between the particles by an increase in valency. Thus the loose-packed but bivalent BaO is as hard as the close-packed but univalent LiF; BaS is as hard as LiCl, and so on.

Solubility.—The chief property by which the heavy metal sulphides are distinguished from those of the alkali and alkaline earth metals is their low solubility. Actually these sulphides are among the most insoluble of all substances; *e.g.* Ag_2S is the least soluble of the silver compounds; even AgI dissolves to a greater extent. Ag_2S does, however, dissolve somewhat in KCN solution, because the complex ions $(Ag(CN)_2)'$ yield such an excessively small quantity of silver ions that even the minute solubility product of Ag_2S is not reached. HgS, the most insoluble sulphide, does not dissolve in KCN. The addition of iodides, however, prevents the precipitation of HgS in acid solution, owing to the extreme stability of the complex ion $[HgI_4]''$. Tl_2S, like TlOH, gives an alkaline solution and is fairly soluble.

The solubility products of some sulphides (mostly according to Bruner and Zawadski [1]) are as follows:—

$$[Mn\cdot\cdot] \times [S''] = 1\cdot4 \times 10^{-15}$$
$$[Fe\cdot\cdot] \times [S''] = 1\cdot5 \times 10^{-19}$$
$$[Tl\cdot]^2 \times [S''] = 4\cdot5 \times 10^{-23}$$
$$\beta \quad [Zn\cdot\cdot] \times [S''] = 1\cdot2 \times 10^{-23}$$
$$[Ni\cdot\cdot] \times [S''] = 1\cdot4 \times 10^{-24}$$
$$[Co\cdot\cdot] \times [S''] = 3\cdot0 \times 10^{-26}$$

$$[Cd\cdot\cdot] \times [S''] = 3\cdot6 \times 10^{-29}$$
$$[Pb\cdot\cdot] \times [S''] = 4\cdot2 \times 10^{-28}$$
$$\text{to } 5 \times 10^{-29}$$
$$[Cu\cdot\cdot] \times [S''] = 8\cdot5 \times 10^{-44}$$
$$[Cu\cdot]^2 \times [S''] = 2 \times 10^{-47}$$
$$[Ag\cdot]^2 \times [S''] = 1\cdot6 \times 10^{-49}$$
$$[Hg\cdot\cdot] \times [S''] = 2 \times 10^{-49}$$
$$\text{to } 4 \times 10^{-52}$$
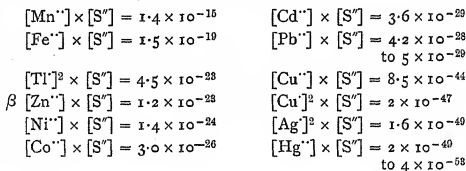
Free acetic acid contains sufficient H-ions to dissolve the sulphides of Fe, Mn and UO_2; but the sulphides of Tl, Zn, Ni and Co are precipitated in acetic acid solution, and zinc sulphide in the presence of sulphuric acid when the solution is very dilute. If the solution is concentrated, while keeping the quantity of acid constant, more ZnS dissolves. The explanation is that the quantity of sulphuretted hydrogen held in solution by the smaller bulk of liquid is proportionately less, while the dissociation of the acid is scarcely reduced; therefore, owing to mass action, the sulphuric acid drives back the dissociation of H_2S further in the concentrated than in the dilute solution. Instead of artificially adding acid, H_2S may be passed through the solution of metallic salt. The mineral acid formed by double decom-

[1] *Z. anorg. Chem.*, 1910, 67, 454.

position opposes the precipitation of sulphide, and the greater the concentration of the salt, and therefore of the H-ions which are formed, the less the quantity of sulphide thrown down; *e.g.* H_2S precipitates 0·0864 of the zinc from a solution of 1 g. $ZnSO_4$ in 1·575 g. water, and 0·510 of the zinc when the solution is diluted to 76·95 g. water.[1]

The sulphides of heavy metals not yet mentioned are much more insoluble in acids; very concentrated acids, however, prevent the precipitation of most of them. HgS and As_2S_3 are not affected by the strongest H-ion concentrations. Mercury sulphide dissolves only when exposed to the oxidising and solvent action of *aqua regia*, and this method is used in analysis. This sulphide is also attacked by concentrated sulphuric acid with formation of a white substance, of which the exact composition is unknown. The insolubility of arsenious sulphide in concentrated hydrochloric acid provides a method of separation from the sulphides of antimony and tin. The sulphides of platinum and of tervalent gold are slightly soluble in acids; PtS_2 dissolves in concentrated acids, Rh_2S_3 and OsS_4, only in *aqua regia*. Vanadium sulphides are also very insoluble. For the solubility of heavy metal sulphides in alkalis and alkali sulphides see p. 537 *et seq.*

The sulphides of aluminium, chromium, titanium, zirconium, niobium, tantalum and thorium are not precipitated by hydrogen sulphide even from alkaline solutions. TiS, Ti_2S_3, TiS_2, ThS_2, ZrS_2, Zr_2S_5 and Zr_2S_3 can be obtained in the dry way; TiS_2 is decomposed only by acids and not by water.

Many sulphides of heavy metals form colloidal solutions (for those of As and Sb, *cf.* p. 740). These are often obtained by passing sulphuretted hydrogen for a long time through suspensions of the precipitated and well-washed sulphides in water; *e.g.* CdS, CuS, GeS_2, MoS_3. Another method is by the precipitation of sulphides from solutions so dilute that the quantity of electrolytes present is not enough to cause coagulation of the sols. Many of these colloids are very stable towards electrolytes. Thus, no precipitation is produced when H_2S is passed through a solution of $KAuCl_2$, or a very dilute one of tartar emetic, until free acid has been added. Colours of colloidal solutions are generally similar to those of the solid sulphides, thus Sb_2S_3 is orange, CdS, As_2S_3, In_2S_3 yellow. Black sulphides often give brown colloidal solutions.

Effect of Heat on Sulphides.—Few metallic sulphides are volatile at moderate temperatures. Those of metals belonging to Group II of the periodic system, ZnS, CdS, HgS, can be sublimed. HgS, which is especially volatile, sublimes at 446°, CdS at 980°, both at atmospheric pressure. The sulphides of arsenic and antimony (see p. 739 *et seq.*) and of tin and lead can also be volatilised. SnS distils at 1090°, SnSe at a white heat, both giving green vapours, while lead sulphide begins to sublime at 660° in the cathode vacuum, and at 860° in a hydrogen atmosphere, at normal pressure. The following are the melting points of some sulphides:

	Sb_2S_3	Ag_2S	SnS	PbS	Cu_2S	MoS_2	MnS
M.pt. . .	550°	825°	880°	1120°	1135°	1185°	>Fe

[1] Ostwald, *J. prakt. Chem.* (2), 1879, 19, 468.

The melting points of the selenides are not very different; *e.g.* SnSe melts at 860°.

The decomposition of sulphides generally takes place at very high temperatures. Even the sulphides of noble metals are fairly stable; *e.g.* Ag_2S must be heated to 810° in a vacuum tube before it decomposes. CuS decomposes at 400° *in vacuo*, giving Cu_2S; the further decomposition $\longrightarrow Cu + S$ requires a very high temperature. The sulphides MoS_3, WS_3, V_2S_5 and PdS_2 also break down when heated, giving the lower sulphides MoS_2, WS_2, V_2S_3 and Pd_2S respectively. These decompositions take place more readily in the presence of hydrogen. Thus CuS heated in hydrogen to 265° rapidly passes into Cu_2S, while in carbon monoxide even a temperature of 130° is sufficient. The sulphides CrS, GeS, VS, etc., are obtained by heating the higher sulphides in hydrogen. The reaction of Ag_2S in hydrogen is interesting; an equilibrium $Ag_2S + H_2 \rightleftharpoons 2Ag + H_2S$ is set up, which can be approached from either side. At 360° equilibrium is reached in about 160 hours, at 580° in a few minutes.

For other metallic sulphides the position of the equilibrium $MS + H_2 \rightleftharpoons M + H_2S$ has been determined by finding the decomposition in a stream of the gas.[1] The following table gives the pressure of sulphur vapour in logarithms of atmospheres. The analogy with the electrometric series is greatest at low temperatures.

Temp.	Ag_2S	Cu_2S	ZnS	HgS	SnS	PbS	As_2S_3	Sb_2S_3	Bi_2S_3	MnS	FeS	Co_4S	Ni_3S_2
440°	...	...	...	-5.36	...	...	-5.24	-6.93	-6.27	...	...	...	...
515°	...	...	...	...	-10.76	-10.73	...	-5.88	-5.10	...	...	...	...
540°	-6.73	...	...	-3.58	...	...	...	-5.5	...	...	...	...	...
610°	...	...	...	...	...	...	-2.86	-4.92	...	...	...	-9.35	...
630°	-6.06	...	...	...	-9.2	-8.98	...	...	...	...	...	...	-9.66
730°	-5.3	...	>-10.8	...	...	...	...	...	...	...	-9.15	-8.08	...
910°	-4.06	-7.16	...	...	...	...	...	...	...	...	-7.09	...	...
1100°	-2.82	...	...	...	...	...	...	...	...	-9.23	-4.51	...	...

Higher sulphides often decompose spontaneously into lower sulphides and sulphur. Thus cupric sulphide precipitated by H_2S breaks down in KCN solution, giving KCNS, owing to the liberation of free sulphur by the formation of Cu_2S and S. Cupric sulphide is similarly unstable in Na_2S solution unless it is saturated with sulphur —otherwise polysulphides and Cu_2S are formed. The equilibrium $2CuS \rightleftharpoons Cu_2S + S$ obtains in such solutions, and consequently it is possible to obtain pure Cu_2S by the use of other substances which remove sulphur, *e.g.* sulphites or arsenites.

Some sulphides are unstable at low temperatures with production of the metal and a higher sulphide; *e.g.* Hg_2S decomposes into HgS + Hg. On the other hand, when sulphuretted hydrogen is passed through a thallic salt a soft fusible substance is formed, which is a mixture of

[1] K. Jellinek and J. Zakowski, *Z. anorg. Chem.*, 1925, 142, 1.

a lower sulphide with free sulphur. Direct union of metals and sulphur by fusion occasionally gives the lower sulphide; from tin and sulphur SnS and not SnS_2 is formed; to obtain mosaic gold (SnS_2) some tin compound must be fused with sulphur; e.g. $SnCl_2$ or a mixture of SnO_2 and NH_4Cl. Very often, however, the higher sulphides can be prepared only in the dry way; Au_2S_3 cannot be obtained in the pure state by precipitation, because it reacts with undecomposed auric salt to give metallic gold according to the equation[1] $Au_2S_3+6(AuCl_4)H+12H_2O \longrightarrow 8Au+3H_2SO_4+24HCl$. It may, however, be obtained in the dry way, but is not very stable, and at 200° part of the gold is liberated; it also leaves a residue of gold when treated with nitric acid.

The sulphides of heavy metals, like the alkali derivatives, are oxidised when heated in the air. The oxidation is often considerable at ordinary temperatures, and is a source of error in analytical processes. Very finely divided sulphides are pyrophoric; e.g. precipitated manganese sulphide which has been dried in vacuo glows when exposed to air.

Phosphorescent Minerals.—Colourless metallic sulphides of a particular crystalline structure, which can be produced by strong heating, possess the property of shining in the dark after a previous exposure to the light. Zinc sulphide (Sidot's blende) is much used in the production of luminous paints, as it is less affected by the air than any other colourless sulphide. The strongly ignited alkaline earth sulphides are, however, nearly as stable, and calcium sulphide is the basis of Balmain's luminous paint. The sulphide is made by heating natural calcium carbonates (e.g. that from ostracite shales, etc.) which either contain sulphur or to which sulphur compounds have been added. These phosphorescent materials are also obtained by reduction of the sulphates. They possess a brilliant phosphorescence which is strongest just after exposure to light, and then slowly diminishes in intensity; the effect lasts for several hours when the best minerals are used. The luminosity becomes permanent without any exposure to light if a little radioactive material is added to the paint. The figures on luminous watches are mostly treated with zinc blende containing a minute quantity of a radium or mesothorium salt. The pure sulphides do not phosphoresce, and the phenomenon depends on the presence of minute quantities of heavy metal salts, e.g. Bi or Mn salts. These impurities also impart colour to the phosphorescence, which may be orange, yellow, blue or green according to the nature of the metallic salt. These sulphides, especially zinc blende, are used in the preparation of luminous screens for radioactive work. Phosphorescence is not confined to metallic sulphides; silicon sulphide also shows this phenomenon but is activated only by carbon. The luminescence of powdered fluorspar is influenced by temperature, and when it is sprinkled over a hot iron plate the light becomes very bright, but dies away quickly. The activity of the sulphides is affected by mechanical treatment, and they phosphoresce with a greater intensity when ground in a mortar. Such luminescence caused by friction is termed triboluminescence; many types of crystalline compounds possess this property. Crystals of arsenic trioxide, potassium sulphate, sugar and many others, which are otherwise not phosphorescent, become luminous by rubbing the crystals together or by crushing them in the dark. The reverse method of constructing the crystals by recrystallisation from solution also causes the phenomenon (crystallo-luminescence). The causes of these various phenomena cannot be discussed here.[2]

[1] Gutbier and Dürrwächter, Z. anorg. Chem., 1922, 121, 266.
[2] Cf. P. Pringsheim, Fluorescenz und Phosphorescenz, Berlin, 1928.

Thiosalts.—Just as acidic oxides unite with basic oxides, giving oxysalts, the metallic sulphides can combine with the sulphides of more negative elements, forming sulpho- or thio-salts :

$$3Na_2O + P_2O_5 \longrightarrow 2Na_3PO_4 \quad K_2O + As_2O_5 \longrightarrow 2KAsO_2 \quad Na_2O + SnO_2 \longrightarrow Na_2SnO_3.$$
$$3Na_2S + P_2S_5 \longrightarrow 2Na_3PS_4 \quad K_2S + As_2S_5 \longrightarrow 2KAsS_2 \quad Na_2S + SnS_2 \longrightarrow Na_2SnS_3.$$
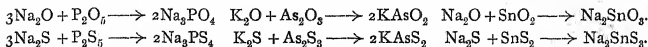
Seleno-salts are also known. The following sulphides have a strong tendency to form the negative components of thiosalts :

$$P_2S_3 \qquad P_2S_5 \qquad As_2S_3 \qquad As_2S_5 \qquad Sb_2S_3 \qquad Sb_2S_5 \qquad TeS_2$$
$$V_2S_5 \qquad MoS_3 \qquad WS_3 \qquad SnS_2 \qquad HgS \qquad Au_2S$$
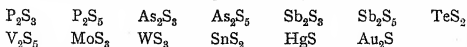
Molybdenum gives salts of polyacids, *e.g.* insoluble compounds of the type $M_2S,3MoS_3$ (but not thioparamolybdates), as well as the salts of the acid H_2MoS_4. Tin gives crystalline salts [1] of the formulae M_2SnS_3 and M_4SnS_4, but similar derivatives of bivalent tin are unknown. The sulpho-tellurites are interesting, and have the formula $3R_2S,TeS_2$. They are formed, together with free tellurium and sulphur, when sulphuretted hydrogen is passed through a solution of a tellurite : $3R_2TeO_3 + 9H_2S \longrightarrow R_6TeS_5 + 2Te + 4S + 9H_2O$. Some of the thiosalts of heavy metals found in nature have a similar structure (*cf.* below). The alkali thio-tellurites are very soluble in water.

Germanium, copper and metals of the platinum group give some thiosalts, although complete series are unknown, while thiosalts of iron, chromium, manganese, silver, etc., can be obtained in the dry way.

The thiosalts are produced either by fusing together the components, or when a solution of the acidic sulphide is treated with the basic sulphide : $Sb_2S_3 + Na_2S \longrightarrow 2NaSbS_2$. A third method consists in passing hydrogen sulphide through a solution of the oxysalt : $NaAsO_2 + 2H_2S \longrightarrow NaAsS_2 + 2H_2O$. Very often intermediate compounds are formed by this process ; *i.e.* oxy-thiosalts, in which only part of the oxygen is replaced by sulphur. Salts of the following acids have been prepared :

$$H_3AsS_4 \qquad H_3AsS_3O \qquad H_3AsS_2O_2 \qquad H_3AsSO_3 \qquad H_3AsO_4$$
$$H_2WS_4 \qquad H_2WS_3O \qquad H_2WS_2O_2 \qquad H_2WSO_3 \qquad H_2WO_4$$
$$H_2MoS_4 \qquad \qquad H_2MoS_2O_2 \qquad H_2MoSO_3 \qquad H_2MoO_4$$
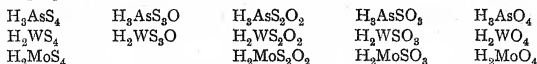
Similar derivatives of vanadium have been prepared, but antimony shows little tendency to form oxy-thiosalts, while such compounds of tervalent arsenic are not known with certainty. Selenium can replace oxygen or sulphur ; examples of these salts are :—

$$Na_3AsO_2Se \qquad\qquad Na_3AsO_2Se_3 \qquad\qquad Na_3AsSSe_3$$
$$Na_3AsO_2SSe \qquad\qquad Na_3AsS_2Se_2 \qquad\qquad Na_3AsS_2Se, \text{ etc.}$$
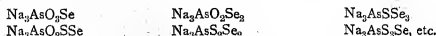
These compounds are sometimes produced in very dilute solution, but if the acidic sulphide is easily hydrolysed they are only stable in concentrated solution ; on dilution, H_2S is given off. The thiosalts of phosphorus behave in this way ; *e.g.* Na_3PS_4 is not stable in dilute solution and splits up into Na_2S and P_2S_5 ; the latter then reacts with water to give phosphoric acid and sulphuretted hydrogen. These thiosalts are therefore prepared in the dry way, and recrystallised from a concentrated solution of alkali sulphide, in which dissociation is largely prevented.

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[1] For thiostannates see Jelley, *J. Chem. Soc.*, 1933, 1580 ; 1934, 1076.

The salts $K_2S.2FeS$, $K_2S.3MnS$, $KCrS_2$ (*i.e.* $K_2S.Cr_2S_3$) or $NaCrS_2$ are obtained in the dry way by fusion of a mixture of the components. By heating the alkali compounds with salts of bivalent heavy metals, well-defined derivatives of the type $M^{II}(CrS_2)_2$, in which M may stand for Zn, Cd, Cu, Sn, Pb, Fe, Co, Ni, Mn, and also for 2Ag. They are almost insoluble in water, and are related to many sulphosalts found in nature; *e.g.* $3ZnS.FeS$; $4Ag_2S.GeS_2$ (argyrodite), compounds of Au_2S_3 with sulphides of arsenic, molybdenum, antimony and bismuth. By heating it with concentrated Na_2S solution Ag_2S can be transformed into a red crystalline compound, $Na_2S.3Ag_2S_3.2H_2O$, which is almost insoluble in alkali sulphides.

The separation of the metals Sn, As, Sb, Au, Pt and Ge from the group precipitate in qualitative analysis depends upon the fact that they dissolve in ammonium sulphide, forming thiosalts. These sulphides also dissolve in alkali hydroxides and even in carbonates, giving either oxy-thiosalts or a mixture of oxysalts and thiosalts. The solubility in ammonium carbonate is very slight except for arsenic sulphide, which dissolves readily, and may thus be separated from the other sulphides. If bivalent Sn or Ge is present the group precipitate must be treated with a polysulphide, usually yellow ammonium sulphide, in order that the metals may be oxidised to soluble quadrivalent salts:

$$SnS + (NH_4)_2S_2 \longrightarrow (NH_4)_2SnS_3 \qquad GeS + (NH_4)_2S_2 \longrightarrow (NH_4)_2GeS_3.$$
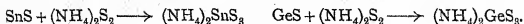
Hence when the brown stannous or germanous sulphides are dissolved in a polysulphide and the solutions acidified, the yellow stannic or white germanic sulphides are thrown down. The free thio-acids are unstable, decomposing at once with evolution of sulphuretted hydrogen: $H_2SnS_3 \longrightarrow H_2S + SnS_2$. The metallic sulphide may be precipitated at once, but in some instances a colloidal solution is produced, from which the sulphide is precipitated very slowly. Such colloidal solutions are best coagulated by warming, and, to avoid loss of H_2S, a closed flask is used. This process is employed in the quantitative determination of molybdenum; the solution containing the colloidal sulphide is acidified and then saturated with sulphuretted hydrogen; it is next transferred to a pressure-flask and placed in a water-bath, which is kept at the boiling point until the MoS_3 has completely separated. Before filtration the excess of H_2S is removed by bubbling air through the liquid, as it would act as a peptising agent (*cf.* pp. 102, 818). A similar precaution is taken with As_2S_3 and Sb_2S_3.

Mercury sulphide is soluble in concentrated Na_2S or K_2S, but only slightly in $(NH_4)_2S$, probably because the ammonium salt is at once hydrolysed. A few sulphides, including those of Cu and Ni, are more soluble in ammonium sulphide than in alkali sulphides. $(NH_4)_2S$ almost invariably contains polysulphides, and these metals

form ammonium salts of poly-sulphoacids very easily. Platinum sulphide is soluble in pure $(NH_4)_2S$, but more so when polysulphides are present; only polyacid derivatives have been isolated (*cf.* below and p. 541). For phosphorus derivatives, see pp. 737, 741.

The sulphosalts and their solutions are red, yellow, brown or colourless. The mercury and tin salts are colourless, those of tellurium and tungsten a pale yellow, the oxy-thiosalts of molybdenum a darker yellow, while vanadates and molybdates in which the whole of the oxygen has been replaced by sulphur are red; in these compounds the valencies of V and Mo may be less than 5 and 6 respectively. The phosphorus derivatives are yellow, and those of gold orange, while the arsenic and antimony salts are mostly yellow, but sometimes red or brown. The naturally occurring thio-antimony salts are, however, black. The solution of PtS_2 in $(NH_4)_2S$ is reddish brown. The selenium derivatives are invariably darker than the corresponding sulphur compounds. All the alkali thiosalts prepared in the wet way dissolve in water and crystallise well—most of the alkaline earth salts are also soluble. The compounds of the heavy metals are precipitated from these solutions by double decomposition.

Polysulphides.—Sulphides of metals which have a large atomic volume combine with more sulphur, giving polysulphides, which may be compared with the polyhalides, formed additively by the same metals (*cf.* p. 243 *et seq.*). The polysulphides and polyhalides probably have a similar structure. The persulphides are not much like the peroxides, for the latter class is confined to derivatives of H_2O_2, while the persulphides are derived from various types, H_2S_x, in which x has a wide range of values.

As in the polyhalides, the alkali metals, especially caesium, form the most stable compounds; next in order of stability are the persulphides of the alkaline earth metals. Certain alkaloids, such as strychnine and brucine, give very stable persulphides. The persulphides are more stable than the polyhalides; hydrogen iodide can only unite with iodine in solution, and no solid compounds can be isolated, while persulphides of hydrogen, although rather easily decomposed, exist in the solid state. A few polysulphide derivatives of the heavy metals exist, mostly as thiosalts (*cf.* p. 541).

"Liver of sulphur," obtained by fusing alkali carbonates with sulphur, contains polysulphides (see p. 525). The soluble polysulphides of the alkalis and alkaline earths are best prepared by treating a solution of the simple sulphide or hydrosulphide with sulphur, which gradually dissolves and imparts to the liquid a yellow or brownish-red colour, which deepens when the solution is concentrated. The concentration of the alkali sulphide solution determines to a large extent the quantity of sulphur that can be absorbed. Definite chemical compounds are not often formed in these solutions, and pentasulphides are not

end-products, as was formerly supposed.[1] The absorption of sulphur proceeds fairly quickly until a composition corresponding to M_2S_4 is reached, and then very slowly, being much influenced by concentration. The equilibrium values of x in the formula Na_2S_x have been determined for various concentrations of Na_2S solution:

Normality of solution .	0·5	0·25	0·125	0·062	0·031	0·016	0·008
Values of x . .	4·98	5·11	5·22	5·24	5·20	5·03	4·46

The point of maximum absorption which here occurs with the 0·062 N solution depends upon the extent of hydrolysis and the degree of dissociation; *e.g.* it is displaced by the addition of NaCl.

The solution evidently contains equilibrium mixtures such as are also present in the fused compounds, and single components are readily isolated by taking advantage of differences of solubility, volatility, etc. For instance, Pearson and Robinson[2] isolated $Na_2S_2 . 6H_2O$; $Na_2S_3 . 8H_2O$; $Na_2S_4 . 8, 9$ and $11 H_2O$; $Na_2S_5 . 6H_2O$. Excluding for the present the polysulphides of heavy metals, compounds of the alkali metals which range as high as M_2S_5 are known; an ammonium derivative $(NH_4)_2S_9$, as well as lower persulphides, has been prepared, and of the alkaline earth metals compounds up to MS_4 have been obtained, of which the barium and strontium sulphides crystallise from solution. The solid polysulphides are well-crystallised substances, but all except Cs_2S_5 are very hygroscopic and are somewhat readily attacked by the oxygen of the air when moist. They are of course decomposed by water with the establishment of equilibria between sulphur and lower sulphides. The intermediate persulphides have a yellow colour, but the higher members are dark yellow or orange red; $(NH_4)_2S_3, 4H_2O$ is ruby-red, and $(NH_4)_2S_9$ is dark red. "Liver of sulphur" appears brown or even green, but this is due to its variable composition and to colloidal coloration. The persulphides are decomposed by acids with liberation of sulphur; *e.g.* $Na_2S_5 + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S + 4S$. Under certain conditions the reaction goes differently, and interesting persulphides of hydrogen are formed.

Hydrogen Persulphides.—The compounds H_2S_2 and H_2S_3 have been isolated,[3] and higher sulphides probably exist; *e.g.* H_2S_4, H_2S_6, etc.[4] If a concentrated solution of alkali polysulphide is poured into aqueous hydrochloric acid, a yellow oil separates, which consists of a mixture of hydrogen persulphides. The acid must not be added to the polysulphide. H_2S_2 and H_2S_3 are obtained by distilling the oil, provided no trace of alkali is present; for this reason the apparatus is first steamed out with hydrochloric acid. H_2S_2 can be distilled at normal pressure, and the pure liquid boils at 70·7°, but H_2S_3 must be distilled

[1] Küster and Heberlein, *Z. anorg. Chem.*, 1905, 43, 53.
[2] *J. Chem. Soc.*, 1930, 1473. [3] Bloch and Höhn, *Ber.*, 1908, 41, 1961.
[4] For H_2S_5 see Mills and Robinson, *J. Chem. Soc.*, 1928, 2326.

under reduced pressure and boils at 69° under a pressure of 2 mm. Both compounds are bright yellow, but become colourless at very low temperatures; H_2S_3 solidifies to a mass of white crystals at $-52°$, while H_2S_2 freezes at $-89°$. For comparison, it may be repeated that H_2S liquefies at $-60\cdot1°$, and solidifies at $-82\cdot9°$. The densities of the liquid compounds also form a sequence:

Density of liquid H_2S: $0\cdot964$ H_2S_2: $1\cdot334$ H_2S_3: $1\cdot496$.

The smell of hydrogen persulphide is more pungent than that of sulphuretted hydrogen; it irritates the mucous membrane. H_2S_3 possesses an odour similar to sulphur chloride and camphor, and is more stable than H_2S_2. It can be kept at room temperature in the dark for days without apparent change; actually some decomposition does occur, and a super-saturated solution of H_2S is produced; the gas is given off with violence if the liquid is shaken. H_2S_3 decomposes more quickly in daylight, especially when warmed, and rhombic crystals of sulphur are deposited. H_2S_2 dissolves large quantities of sulphur, but the freezing point curves give no indication of the formation of compounds of higher sulphur content. Solutions of sulphur in H_2S_3, however, contain at least one higher polysulphide, $H_2S_3 . 3S$, which points to a difference in structure between the disulphide and the trisulphide, possibly analogous to that between dithionic and trithionic acids. All the hydrogen persulphides, when heated, split up into mixtures of higher and lower sulphides similar to those present in alkali sulphide solutions. When H_2S_3 is distilled under normal pressure, one-third of the liquid is converted into the volatile H_2S_2, and hence the non-volatile residue contains higher persulphides than H_2S_3. The two sulphides burn with a blue flame; they are oxidised when exposed to air, with formation of free sulphur. The compounds are at once decomposed by water, a white precipitate of sulphur being produced; this decomposition is retarded by hydrochloric acid, but accelerated by traces of alkalis. The persulphides are also attacked by alcohol, but dissolve without decomposition in CS_2, C_6H_6 and ether.

The persulphides are stronger acids than sulphuretted hydrogen, in accordance with Abegg and Bodländer's theory (cf. p. 618); the increase in acidity is shown by the progressive decrease in the hydrolysis of alkali persulphides as the sulphur content becomes greater. According to Küster and Heberlein the hydrolysis of the sulphides in $0\cdot1$ N solution is:

	Na_2S	Na_2S_2	Na_2S_3	Na_2S_4	$Na_2S_{5\cdot22}$	$NaHS$
Per cent. hydrolysis .	86·4	64·6	37·6	11·8	5·7	0·15

The polysulphides of the heavy metals usually exist in combination with alkali sulphides as thiosalts. Derivatives of copper, platinum, gold, and possibly of other metals, are known. The copper compounds of the type $M'[CuS_4]$ possess a beautiful

deep red colour; the ammonium salt is obtained when a solution of $CuSO_4$ is poured into conc. $(NH_4)_2S_5$, alcohol added, and the liquid left to crystallise. The alkali salts are prepared by adding alkali hydroxides to this solution. If, however, too little alcohol is used, a black compound, $M_2Cu_9S_{10}$, is formed instead of the red salt.[1] A yellow compound, NH_4AuS_3, and a red derivative, $(NH_4)_2PtS_{15}, 2H_2O$, have also been obtained.[2] These compounds are transparent, while the sulphides are quite opaque. The black, crystalline product which is obtained when a solution of NiS in ammonium polysulphide is allowed to stand for several days probably belongs to this class of compounds; the substance is certainly rich in sulphur, but it is doubtful whether it contains ammonia. It is well known that precipitated nickel sulphide easily forms a dark brown colloidal solution, provided that ammonia and hydrogen sulphide are both present in excess.[3] If the liquid is very rich in sulphur, the nickel compound is obtained in the solid state.

A dark reddish brown lead disulphide, PbS_2, which is free from alkali, is obtained by the action of sulphur on butyl lead mercaptide.[4] As this substance gives H_2S_2 when treated with hydrochloric acid, it must be a true persulphide of bivalent lead.

Little is known of the polyselenides; they resemble the polysulphides, but are darker in colour.

Basic Thiosalts.—These compounds are the sulphur analogues of basic and imino-basic salts (*cf.* p. 625 *et seq.*), in which the O atom or NH group is replaced by the S atom; *e.g.* :—

Basic salt	.	.	.	$ClM.O.MCl$
Thiobasic salt	.	.	.	$ClM.S.MCl$
Amino-basic salt	.	.	.	$ClM.NH.MCl$

The formation of thiobasic salts is similar to that of ordinary basic salts; the normal salts are treated with H_2S instead of H_2O, causing a kind of "sulphur hydrolysis": $2MCl_2 + H_2S \rightleftharpoons M_2SCl_2 + 2HCl$. With excess of H_2S, the reaction proceeds further, giving the normal sulphide: $M_2SCl_2 + H_2S \rightleftharpoons 2MS + 2HCl$. Mercuric and lead salts have a strong tendency to form basic thiosalts. When H_2S is passed through solutions of mercury salts, the first precipitate formed is white; it then becomes yellow, brown and finally black. The intermediate colour with lead salts is red; all these colour changes are due to basic salts. Like the oxy-basic salts, the composition of these substances is very varied and has not been definitely determined; it depends on the concentration of the solution. Compounds of the type $2HgS$, HgX_2 may serve as examples of these thiobasic salts. They have a white or yellow colour, and X may stand for Cl, Br, I, F or SO_4. The chloride compounds are termed thiochlorides, etc. Other types are also known, *e.g.* $Hg(HgS)SO_4$ and $[Hg(HgS)_2]Cr_2O_7$, which have characteristic X-ray diagrams.

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[1] H. Biltz and Herms, *Ber.*, 1907, 40, 974.
[2] Hofmann and Höchtlen, *Ber.*, 1903, 39, 3090.
[3] Thorne and Pates, *Kolloid-Z.*, 1926, 38, 155.
[4] Duncan and Ott, *J. Amer. Chem. Soc.*, 1931, 53, 3940.

OXYGEN COMPOUNDS OF SULPHUR, SELENIUM AND TELLURIUM

Sulphoxylic acid—Hyposulphurous acid—The dioxides—Sulphurous (selenious, tellurous) acid—Thiosulphates—Dithionic acid—The higher polythionic acids—The trioxides of sulphur and tellurium—Sulphuric acid

THESE three elements all form dioxides corresponding to SO_2 and trioxides corresponding to SO_3, and these anhydrides by addition of water give the -ous and -ic acids respectively, of which sulphurous and sulphuric acids, H_2SO_3 and H_2SO_4, are examples. Telluric acid combines with more water to give the tetra- and hexa-basic acids H_4TeO_5 and H_6TeO_6. No other oxides or oxyacids of selenium and tellurium are known; TeO has been described; it was prepared by heating[1] tellurium-sulphur sesquioxide, $TeSO_3$, but according to Damiens[2] it is a mixture of Te and TeO_2. Sulphur, however, readily forms a monoxide, SO, a tetroxide, SO_4 or S_2O_8, which is probably the anhydride of Caro's acid, and a heptoxide, S_2O_7, the anhydride of persulphuric acid, $H_2S_2O_8$, as well as a large number of acids. Disulphur monoxide, S_2O, also exists. In the following list an asterisk denotes that only salts or other derivatives are known, and that the acid itself does not exist or has only a transitory existence.

H_2SO_2*	$H_2S_2O_4$*	$H_2S_2O_3$*
Sulphoxylic acid.	Hyposulphurous acid.	Thiosulphuric acid.
$H_2S_{2-6}O_6$	$H_2S_2O_8$	H_2SO_5
Di—hexa-thionic acids.	Perdisulphuric acid.	Caro's acid.

The constitutions of the oxides and oxyacids of this group present considerable difficulties and the possibility of resonance must not be overlooked.

Sulphoxylic acid, H_2SO_2 or $S(OH)_2$.—This is the least well known of the sulphur acids. Bassett and Durrant[3] consider that this acid is formed in the first stage of the hydrolysis of sulphur, $2S + 2H_2O \rightleftharpoons H_2S + S(OH)_2$, the reaction being comparable with the hydrolysis of chlorine and of phosphorus. The zinc salt is formed by the interaction of zinc and sulphuryl chloride in ethereal solution : $SO_2Cl_2 + 2Zn \longrightarrow ZnCl_2 + ZnSO_2$ or by the action of SO_2 on granulated zinc in absolute alcohol. $CoSO_2 . xH_2O$ is obtained by the interaction of $CoCl_2$ and $Na_2S_2O_4$ in presence of ammonia.[4] The free acid is not known, but organic derivatives have been

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[1] Doolan and Partington, *J. Chem. Soc.*, 1924, **125**, 1402.
[2] *Compt. rend.*, 1924, **179**, 829.   [3] *J. Chem. Soc.*, 1927, 1401.
[4] Scholder and Denk, *Z. anorg. Chem.*, 1935, **222**, 17.

prepared, e.g. $2C_6H_5CH_2Cl + ZnSO_2 \longrightarrow (C_6H_5CH_2)_2SO_2 + ZnCl_2$. An addition product of the acid sodium salt and formaldehyde ("Rongalite") crystallises from an aqueous solution containing $Na_2S_2O_4$ and HCHO. The essential change is given by the equation $Na_2S_2O_4 + H_2O \longrightarrow NaHSO_2 + NaHSO_3$.[1] The formulæ

$$H . SO . OH \quad \text{and} \quad H . CH\begin{matrix}OH\\O . SONa\end{matrix}$$

have been suggested for the acid and for Rongalite. The unstable ester $S(OC_2H_5)_2$ is obtained from diethylthiosulphite $C_2H_5OS . SOC_2H_5$, and sodium ethoxide in ethyl alcohol; diethylthiosulphite is obtained from S_2Cl_2 and excess of sodium ethoxide.[2]

Sulphur Monoxide, SO.—This oxide[3] is produced in yields not exceeding 40 per cent. and mixed with SO_2 by the combustion of sulphur in air; at a pressure of 5 mm. the optimum yield is obtained (see also p. 569). It is also formed by the thermal dissociation of thionyl chloride or bromide. The oxide, which is a gas at room temperature, dissolves in aqueous alkalis; the solution decolorises indigo and possibly contains sulphoxylate; it converts metals to sulphides. These reactions may, however, only be due to the formation of H_2S and SO_2 when the gas is dissolved in aqueous media.

Hyposulphurous Acid (Dithionous Acid), HSO_2 or $H_2S_2O_4$.

—Salts of this acid are obtained synthetically by passing SO_2 gas through a suspension of the metal in alcohol[4]: $Zn + 2SO_2 \longrightarrow ZnS_2O_4$; or $Na + SO_2 \longrightarrow NaSO_2$. They are also formed[5] when the hydrides of alkali metals are treated with SO_2: $KH + SO_2 \longrightarrow KSO_2 + H$. These methods are not suitable for preparing the large quantities of hyposulphites used in the dye industry as reducing agents, and for this purpose solutions of bisulphites are treated with zinc[6]: $2NaHSO_3 + Zn + SO_2 \longrightarrow ZnSO_3 + 2NaSO_2 + H_2O$. During the reaction an intense orange colour appears which is probably due to the formation of the free acid; the coloration is also noticed when solutions of neutral hyposulphites are acidified, but it quickly disappears, and sulphur is precipitated. The solid sodium salt is obtained from the hyposulphite solution by salting out with a very soluble sodium compound. The salts prepared in this way contain water of crystallisation (the sodium salt two, the potassium salt three and the calcium salt one and a half mols. H_2O), and are so easily oxidised in the air that they are useless for technical processes. They become anhydrous when heated to a moderate temperature, and in this form are much more stable in air, and do not readily recombine with water. The water of crystallisation is removed by warming with alcohol or some other organic liquid which dissolves water, or with concentrated caustic soda to about 70°, after which the salt is washed with a liquid free from water. The sodium salt dissolves slowly in cold water, more quickly in the warm. The cold solution

[1] Bernthsen and Bazlen, *Ber.*, 1900, 33, 126.

[2] Meuwsen and Degel, *Ber.*, 1935, 68B, 121; Meuwsen and Gebhardt, *ibid.*, 1935, 68B, 1011; 1936, 69B, 937.

[3] Schenk, *Z. anorg. Chem.*, 1933, 211, 150; 1934, 220, 268; 1936, 229, 305.

[4] Bernthsen, *Ber.*, 1905, 38, 1048.   [5] Nabl, *Monatsh.*, 1899, 20, 679.

[6] Moissan. *Compt. rend.*, 1902, 135, 647.

has the strongest reducing properties. All the hyposulphites are colourless crystalline compounds.

The hydrated salts are quickly oxidised by the air, and aqueous solutions may be used in gas analysis for absorbing oxygen. The dry, anhydrous salts are stable in air. The salts of heavy metals react with hyposulphites in one of two ways: the noble metals, arsenic, antimony, bismuth and copper, are reduced to the metallic state, and probably a little free sulphur is formed at the same time; these reactions often result in colloidal solutions of the metals, e.g. copper gives a red colloidal solution. The baser metals which form slightly soluble sulphides are quickly reduced to this stage; e.g. lead salts give a white precipitate which soon becomes red, then brown and finally black. Ammoniacal copper solutions are decolorised owing to reduction to cuprous salts, and this reaction can be used for the quantitative estimation of hyposulphites. The bleaching of indigo by hyposulphites is a characteristic reaction. When heated, solutions of hyposulphites are decomposed according to the equation: $2Na_2S_2O_4 + H_2O \longrightarrow Na_2S_2O_3 + 2NaHSO_3$; free hyposulphurous acid probably undergoes a similar decomposition; the disappearance of the orange colour which is produced by acidification of the salts is accompanied by separation of sulphur and a smell of SO_2. Complex hyposulphites, e.g. $FeS_2O_4 . 2py$, $MnS_2O_4 . 2py$, $ZnS_2O_4 . py$ are often more stable than the simple salts.[1]

The empirical formula of hyposulphites was satisfactorily established by Bernthsen.[2]

Various constitutional formulae have been suggested, e.g. $\begin{matrix} NaSO_2 \\ | \\ NaSO_2 \end{matrix}$ i.e. electronically

$$\left[\begin{matrix} \overline{O}^6 & & \overline{O}^6 \\ \overset{+}{S}^2 = & \overset{+}{S}^2 \\ \overline{O}^6 & & \overline{O}^6 \end{matrix} \right]^{++} Na_2 ;$$ the undissociated acid would be $\begin{matrix} O \leftarrow S - O - H \\ | \\ O \leftarrow S - O - H \end{matrix}$. Such
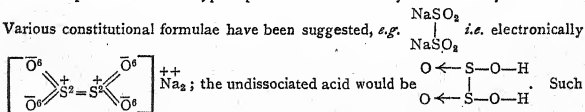
a compound, however, should give a dithionate by oxidation, but, actually, acid sulphites, sulphates and thiosulphates are formed more easily. A second formulation [3]

$$\begin{matrix} NaSO \\ | \\ O \\ | \\ NaSO_2 \end{matrix} \quad i.e. \text{ electronically} \quad \left[\begin{matrix} S^4 = \overline{O}^6 \\ || \\ O^4 \\ || \\ \overline{O}^6 \\ + S^2 \overline{O}^6 \end{matrix} \right]^{++} Na_2 \text{ and the undissociated acid} \quad \begin{matrix} S - OH \\ | \\ O \\ | \\ O \leftarrow S - OH \end{matrix} ,$$
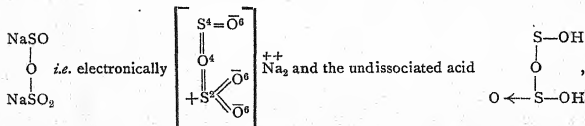
agrees more closely with facts, for example, with hydrolysis to sulphoxylate and sulphite (p. 544). The possibility that the hyposulphites are addition products of the metals with SO_2 cannot be excluded, for metals are known to form addition products with hydrogen and ammonia. The second formulation of the salts, in a sense embraces this idea. Bassett and Durrant[4] consider that the acid consists of a

[1] Scholder and Denk, Z. anorg. Chem., 1935, 222, 41.
[2] Final paper: Ber., 1905, 38, 1048.   [3] Binz, Ber., 1904, 37, 3549.
[4] J. Chem. Soc., 1927, 1401.

coloured co-ordination compound of $S(OH)_2$ and SO_2, *i.e.* $S(OH)_2 \ldots SO_2$ and the second form dealt with above. There is no direct experimental evidence in favour of the double formula $Na_2S_2O_4$.

The Dioxides of Sulphur, Selenium and Tellurium.—These are the most stable of the oxides produced by this group of elements. They are obtained when the trioxides are heated (*cf.* p. 568), that of tellurium with the greatest ease, or by burning the elements in the air. Oxidising agents such as nitric oxide, nitric acid, *aqua regia* or the halogens convert free sulphur to sulphuric acid, in which sulphur is sexavalent, but with selenium and tellurium the oxidation stops at the quadrivalent stage. Thus SeO_2 or TeO_2 is obtained when the element is burned in air in the presence of nitric oxide. A less satisfactory method consists in dissolving selenium or tellurium in nitric acid. TeO_2 is precipitated in the form of small crystals when the tellurium solution is poured into water; it is necessary to evaporate the selenium solution, and SeO_2 can finally be obtained as a sublimate of long white needles.

Sulphur dioxide is usually prepared by burning free sulphur or certain sulphides in air; *e.g.* pyrites, FeS_2, if ignited, burns spontaneously and SO_2 is given off, leaving a residue of ferric oxide. Compounds poorer in sulphur require to be heated, *e.g.* $ZnS + 3O \longrightarrow ZnO + SO_2$. It has already been noted that SO_2 is formed when H_2S is burned in an excess of air: $H_2S + 3O = SO_2 + H_2O$. Thiosulphates decompose on heating with formation of sulphur; hence in a current of air SO_2 is produced.

Sulphur dioxide can also be obtained by reduction of SO_3; in practice sulphuric acid is heated with metals or non-metals:

$$H_2SO_4 + \overset{\text{II}}{R} \longrightarrow H_2SO_3 + RO \qquad H_2SO_3 \longrightarrow H_2O + SO_2.$$
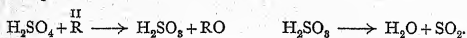
Of the metals, copper and mercury give the best results; if baser metals are employed, side-reactions occur which involve the formation of hydrogen, sulphuretted hydrogen and free sulphur. Zinc and certain varieties of iron, however, give a good yield of SO_2. The metallic oxides which are first formed dissolve in the excess of acid, giving sulphates. The complete reaction is therefore represented by the equation $2H_2SO_4 + M^{II} \longrightarrow M^{II}SO_4 + 2H_2O + SO_2$.

The non-metals which reduce sulphuric acid include carbon and sulphur. When carbon is used, CO_2 is formed in addition to SO_2: $2H_2SO_4 + C \longrightarrow 2SO_2 + CO_2 + 2H_2O$. With sulphur, SO_2 only is evolved: $2H_2SO_4 + S \longrightarrow 3SO_2 + 2H_2O$, but the reaction is slow, as the sulphur melts and attacks the acid only at the interface. Sulphur dioxide is also formed by the reduction of sulphates with sulphides on heating: $ZnSO_4 + ZnS \longrightarrow 2Zn + 2SO_2$. This reaction occurs in the extraction of certain metals from their ores (*cf.* p. 197).

Free sulphurous acid, like carbonic acid, easily decomposes:

$H_2SO_3 \longrightarrow H_2O + SO_2$; the sulphites are attacked by acids with brisk evolution of SO_2. Small quantities of the gas are conveniently prepared in the laboratory by the action of concentrated sulphuric acid on sodium bisulphite solution. The acid is added drop by drop, and a steady stream of SO_2 can be maintained. The preparation of SO_2 by the action of heat on sulphites is not to be recommended. The decomposition $M_2SO_3 \longrightarrow M_2O + SO_2$ is not quantitative; part of the sulphite is changed into sulphide, and part into sulphate, owing to the tendency of sulphur to form sexavalent compounds. If an aqueous solution of SO_2 is heated to 180° in a sealed tube, H_2SO_4 and free sulphur are obtained.

The dioxides of S, Se and Te differ greatly from each other in their physical properties. SeO_2, heated under ordinary conditions sublimes, giving long white needles; but if heated in a closed vessel it melts at 340°. TeO_2 melts at a red heat. SeO_2 is the most soluble of these oxides and mixes with water in almost all proportions; the concentrated solutions are syrupy. TeO_2 is practically insoluble, while SO_2 is a moderately soluble gas (see below). Selenious acid, H_2SeO_3, is stable, and is obtained in the form of large transparent prisms when a concentrated solution of the dioxide is evaporated; the existence of tellurous acid is doubtful, and free H_2SO_3 cannot be isolated, although SO_2 forms a hydrate, $SO_2.7H_2O$, analogous to chlorine hydrate (p. 403). SO_2 is colourless in all three states of aggregation; solid SeO_2 is also white, but when fused it is yellow at 350° and its pungent vapour has a colour similar to that of chlorine. TeO_2 is a white solid which becomes yellow when heated, and melts to a dark yellow liquid; it regains its white colour at ordinary temperatures. TeO_2 exists in two varieties; the common form is composed of small octahedral crystals. The densities of SeO_2 and TeO_2, which are solid at room temperature, are 3·95 and 5·9; liquid SO_2 at a temperature of −20° has a density of 1·49.

Sulphur dioxide is easily liquefied; the gas condenses under normal pressure at −10·1°. At 50° liquid SO_2 has a vapour pressure of 8·4 atmospheres. Sulphur dioxide, in common with other gases which can be readily liquefied, is adsorbed in large quantities by porous substances like charcoal (cf. pp. 184, 612). Liquid SO_2 freezes at −72·7° to a white solid, which has a higher density than the liquid. Liquid SO_2 is but slightly miscible with water. The solubility of gaseous SO_2 per vol. of water is:

Temperature	0°	10°	20°	30°	40°
Vol. SO_2	68·6	51·4	36·2	26·8	17·0

SO_2 and SeO_2 are more soluble in alcohol. One vol. alcohol dissolves 216·5 vols. SO_2 at 0° and 84·2 vols. at 25°. Camphor dissolves more than 300 vols. SO_2 (cf. p. 597). Sulphur dioxide is excessively soluble

in formic acid and in acetone; the former solvent absorbs 351 vols. SO_2, the latter 589 vols. (2·07 times its own weight). Liquid SO_2 does not dissolve free sulphur, but it is miscible with S_2Cl_2 in all proportions. Sulphur dioxide dissolves more readily than HCl in conc. sulphuric acid; about 6 vols. SO_2 dissolve in this acid at room temperature. The density of the aqueous solution is almost independent of the concentration; it is somewhat greater than that of water, in agreement with the fact that liquid SO_2 is rather more dense than water. The density of the saturated solution is:

Temperature	.	.	0°	10°	20°	40°
Density	.	. .	1·061	1·055	1·024	0·995

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in formic acid and in acetone; the former solvent absorbs 351 vols. SO_2, the latter 589 vols. (2·07 times its own weight). Liquid SO_2 does not dissolve free sulphur, but it is miscible with S_2Cl_2 in all proportions. Sulphur dioxide dissolves more readily than HCl in conc. sulphuric acid; about 6 vols. SO_2 dissolve in this acid at room temperature. The density of the aqueous solution is almost independent of the concentration; it is somewhat greater than that of water, in agreement with the fact that liquid SO_2 is rather more dense than water. The density of the saturated solution is:

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TeO_2. The alkali salts are readily formed from solutions of the components. Sulphur dioxide resembles CO_2 in combining very slowly with solid anhydrous metallic oxides; there is scarcely any reaction with the oxides of heavy metals. Selenites and tellurites are obtained when SeO_2 or TeO_2 is fused with metallic oxides. This method is applicable to many of the tellurites which fuse without decomposition. The compounds of the heavy metals are readily obtained by the double decomposition of soluble salts with the alkali sulphites, etc., as the sulphites, selenites and tellurites of these metals are insoluble and in this respect resemble the carbonates. All sulphites of alkali metals and the bisulphites of the alkaline earths dissolve in water, while even the acid selenites and tellurites of the alkali metals are only slightly soluble. In general, all these salts are readily soluble in acids, but the selenites of lead and silver and the sulphites of mercury and silver are remarkable for their slight solubility in nitric acid (see p. 551).

The resemblance between carbonates and sulphites may largely be traced to the similarity of the formulae, H_2SO_3 and H_2CO_3. There are many examples of isomorphism amongst sulphites and carbonates, and corresponding salts often contain the same quantity of water of crystallisation. Lithium sulphite (with 1 and 2 mols. H_2O), however, is quite soluble like the other alkali sulphites, while lithium carbonate is almost insoluble. Sodium sulphite, like sodium carbonate, crystallises with 0, 7 or 10 mols. H_2O; the solubility curve of the former salt reaches a maximum at $33°$, thus resembling Glauber's salt. The anhydrous sulphite begins to separate when the saturated solution is warmed. The sulphites of the other alkali metals, including the ammonium salt, crystallise with small quantities of water like the carbonates, but they are often deliquescent; e.g. the potassium salt crystallises with 0, 1 and 2 mols. H_2O; the ammonium salt with 0 and 1 mol. H_2O. Ammonium bisulphite, NH_4HSO_3, does not exist in the solid state, but the pyro-salt $(NH_4)_2S_2O_5$ sublimes at about $130°$.

Owing to the weakly acidic properties of sulphurous acid, the normal alkali salts are strongly alkaline in solution. The less electropositive metals, Al, Cr, etc., generally give only basic sulphites. Solutions of the acid salts differ from bicarbonates in having a distinctly acid reaction. Solid bisulphites, as well as the solutions, contain free SO_2 and smell strongly of this gas. The sulphites of the alkaline earths and of many heavy metals dissolve in water containing sulphur dioxide, owing to the formation of bisulphites. Only the alkali bisulphites have been isolated; even that of magnesium has not been prepared, although the normal salt is fairly soluble, more so in cold than in hot water (1 part dissolves in 80 parts cold and in 120 parts hot water); very concentrated solutions of some bisulphites can be obtained, e.g. of calcium, though the normal calcium sulphite is soluble with difficulty.

Strontium sulphite (1 part dissolves in 20,000 parts H_2O) and barium sulphite (1 part in 46,000 parts H_2O) are still more insoluble, but the bisulphites of these metals are very soluble.

The hydrolysis of selenites and tellurites is greater than that of the sulphites, in accordance with the weaker nature of the parent acids. Solutions of the tellurites are very unstable; e.g. an acid tellurite breaks down into TeO_2 or into more acid salts which are precipitated, and less acid salts which remain in solution. The dissolved salts form equilibrium mixtures (cf. the molybdates, pp. 512, 514).

Crystalline sulphites are obtained by warming bisulphite solutions, a method not always applicable to the carbonates. Sulphites usually crystallise with water of crystallisation, e.g.:

Ni	Co	Zn	Cd	Mg	Ca	Sr	Ba	salt.
4, 6	3, 5	2, $2\frac{1}{2}$	0, 2	0, 3, 6	2	0, $\frac{1}{2}$	0	mols. H_2O.

Compounds of ammonia with these sulphites and with selenites of heavy metals have been prepared.

Two structures have been proposed for sulphurous acid :

$$\text{I. } O:S:(OH)_2 \text{ or } \left[SO_3\right]H_2 \qquad \text{II. } H.SO_2.OH \text{ or } \left[S^{H}_{O_3}\right]H.$$
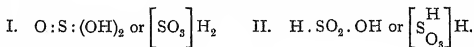
Electronically, these are

$$Ia. \quad \begin{matrix} HO \\ HO \end{matrix} \hspace{-0.5em} \diagdown S \rightarrow O \quad \text{and} \quad IIa. \quad \begin{matrix} H \\ HO \end{matrix} \hspace{-0.5em} \diagdown S \diagup \begin{matrix} O \\ O \end{matrix}$$
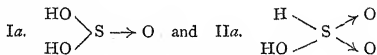
There is evidence in favour of both formulae, for two ethyl sulphites are known and possibly the soluble sulphites exist in both forms. The symmetrical structure I. is supported by the production of $SOCl_2$ when the sulphites are treated with PCl_5. One series of these salts, including those of mercury and silver, are almost insoluble in acids, and are unaffected by the air; they probably have the unsymmetrical structure. The compound $Hg:(SO_3H)_2$ is not mercury bisulphite but a very stable complex derivative in which the mercury atom is directly attached to sulphur. It forms salts of the type $[Hg:(SO_3)_2]R_2$ which ionise thus :

$$[Hg:(SO_3)_2]R_2 \longrightarrow [Hg:(SO_3)_2]'' + 2R\cdot.$$
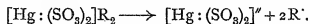
These salts were formerly regarded as double sulphites : $HgSO_3.R_2SO_3$. They are not oxidised by the air, and if excess of a mercuric salt is added to a solution of sulphite the latter is no longer oxidised by permanganate. Another name for the mercury salt is mercurosulphonic acid, as it contains the sulphonic acid radical, $-SO_3H$. This group appears to be present in bisulphites, although the metal does not form part of a strong complex. The bisulphites react with nitrites to give compounds of the type $N(SO_3M)_3$. The sulphites, like

the hypochlorites and nitrites, consist of a mixture of the two isomeric forms in equilibrium with each other. Sometimes one and sometimes the other structure predominates, according to external conditions and the nature of the derivative (cf. pp. 360, 688). The possibility of complex radicals and co-ordination must not be overlooked; the complex nature of the silver and mercury salts has already been described. When a solution of a chromic salt is decomposed with a sulphite the resulting liquid does not give the usual test for chromic salts either in acid or in alkaline solution; obviously the chromium forms part of a complex ion. The presence of a complex salt is sometimes detected by the colour, e.g. cuprous sulphite is colourless, the basic cupric sulphite is yellow, but the cupro-cupric compound Cu_2SO_3, $CuSO_3$, $3H_2O$ gives scarlet crystals and is stable in the air; its pentahydrate, however, resembles the cupric salt and crystallises in yellow flakes. Cupric sulphite is stabilised by co-ordination of the copper, e.g. in [Cu en$_2$]SO$_3$; this is analogous to other cupric compounds of which the unco-ordinated varieties are unknown or unstable, e.g. [Cu en$_2$]I$_2$. H$_2$O or $2H_2O$, [Cu en$_2$]S$_2$O$_3$, [Cu en$_2$](SCN)$_2$ and [Cu en$_2$](H$_2$PO$_2$)$_2$.

Metals of Group VIII of the periodic system, the metals of the first and second subgroups, together with Mn, Mg and Be, form double sulphites, better termed sulphito-salts. The bivalent metals give two series, viz. the type [M^{II}(SO$_3$)$_2$]R$_2$, i.e. MSO$_3$, R$_2$SO$_3$ and derivatives of the formula [M^{II}(SO$_3$)$_4$]R$_6$, i.e. MSO$_3$, $3R_2SO_3$. The sulphito-salts of tervalent elements have the general formula [M^{III}(SO$_3$)$_3$]R$_3$, but gold forms salts of the type [Au^{I}(SO$_3$)$_2$]R$_3$ and [Au^{III}(SO$_3$)$_4$]R. The group SO$_3$″, normally bivalent, behaves as though it had a co-ordination number of one in some compounds, as, for example, the series [M^{II}(SO$_3$)$_4$]R$_6$, unless indeed the co-ordination number of M^{II} is assumed to be 8.

A better example is the compound $\left[Fe{(CN)_5 \atop SO_3} \right]$ Na$_5$; clearly one (CN) group has been replaced by a (SO$_3$) radical. In the series of compounds

I. $\left[Pt{SO_3 \atop Cl_3} \right]R_3$ II. $\left[Pt{(SO_3)_2 \atop Cl_2} \right]R_4$ III. $\left[Pt{(SO_3)_3 \atop Cl} \right]R_5$
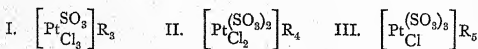
one Cl atom of I. is replaced by (SO$_3$) in compound II., while two of the Cl atoms of I. are replaced in III.

Chemical Properties.—Sulphites, selenites and tellurites possess both oxidising and reducing properties; sulphurous acid generally acts as a reducing and tellurous acid as an oxidising agent. Sulphurous acid is attacked by strong reducing agents. Thus sulphur is formed by its reaction with hydrogen iodide, while the products of electrolytic reduction are either sulphur or hyposulphites according to the conditions of the experiment. Some reducing agents, e.g. hypophosphorous acid, reduce sulphurous acid to hydrogen polysulphide. The following

oxidations by SO_2 (Wardlaw) will also proceed in presence of excess of acid:

$$4FeCl_2 + SO_2 + 4HCl \longrightarrow 4FeCl_3 + 2H_2O + S ;$$
$$4CuCl + SO_2 + 4HCl \longrightarrow 4CuCl_2 + 2H_2O + S ;$$
$$2Hg_2Cl_2 + SO_2 + 4HCl \longrightarrow 4HgCl_2 + 2H_2O + S ;$$
$$3SnCl_2 + SO_2 + 6HCl \longrightarrow 3SnCl_4 + 2H_2O + H_2S.$$
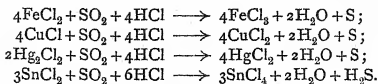
In the reaction between sulphuretted hydrogen and sulphur dioxide the chief product is sulphur: $SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$, but small quantities of polythionic acids are formed at the same time (cf. p. 562 et seq.). SeO_2 and TeO_2 are readily reduced by the reagents which attack sulphur dioxide. When H_2S is passed through SeO_2 solution a characteristic lemon-yellow coloured precipitate is formed; this may be a compound SeS_2, but is more probably a mixture of sulphur $SeO_2 + 2H_2S \longrightarrow Se + 2S + 2H_2O$. The precipitate with TeO_2 is at first red, but rapidly turns black. Mild reducing agents attack SeO_2 and TeO_2; thus glucose effects the precipitation of free selenium and tellurium. Elements which precede selenium and tellurium in the electro-chemical series, such as the metals tin, lead, copper and silver, displace them from acidified solutions of selenites and tellurites. Only tellurium is precipitated by mercury. Nascent hydrogen may be used instead of these metals, and among other reducing agents which attack SeO_2 and TeO_2 are $FeSO_4$, lower acids of phosphorus and stannous chloride. Selenium and tellurium are quantitatively precipitated by hydrazine and by SO_2, and these methods of reduction are employed for the gravimetric determination of the elements.

Sulphites, selenites and tellurites are oxidised to sulphates, etc., by permanganate, halogens, hydrogen peroxide, or by electrolysis, both in acid and alkaline solution. Sulphurous acid is also oxidised by mild oxidising agents, e.g. ferric and some cupric salts. Nitric acid and nitric oxide do not attack SeO_2 and TeO_2, but convert SO_2 to sulphuric acid (see p. 570), or to nitrosylsulphuric acids (see p. 645). Solutions of sulphurous acid and its salts are even oxidised by the air to sulphuric acid and sulphates. The rate of this oxidation is retarded by traces of certain compounds which act as negative catalysts. The following concentrations of various catalysts produce equal effects:

Phenol	Glycerol	Mannitol	Benzaldehyde
1 : 4000	1 : 22270	1 : 23970	1 : 52350

The greatest retardation, however, is caused by $SnCl_2$, and is perceptible at a dilution of 1 mole per 10,000,000 litres. The purer the water used in dissolving the sulphites the more slowly oxidation takes place. The impurities ordinarily present in water therefore have a positive catalytic influence upon the reaction; it is supposed that the addition of a negative catalyst poisons the positive catalyst and so prevents oxidation.

Thiosulphates.—The sulphites are oxidised by free sulphur as well as by oxygen: $M_2SO_3 + S \longrightarrow M_2S_2O_3$. These salts can be obtained in several ways. The aqueous solution of the sulphite may be warmed with sulphur, or a mixture of the solid salt with sulphur heated above the melting point of the element; sulphate, polythionates and polysulphides may also result from this reaction (see pp. 539 and 555). A third method consists in heating sulphur with caustic alkalis. Part of the sulphur is converted into M_2S and part oxidised to M_2SO_3, and the latter unites with unused sulphur, forming thiosulphate. If it is desired to convert the sulphide into thiosulphate, SO_2 is passed through the solution, causing the regeneration of sulphur: $2H_2S + SO_2 \longrightarrow 2H_2O + 3S$. As long as any sulphide remains in solution the liquid turns yellow, due to the formation of polysulphides. The stream of SO_2 is therefore continued till the solution becomes colourless. Using caustic soda, the first reaction may be represented by the equation $6NaOH + 12S \longrightarrow Na_2S_2O_3 + 2Na_2S_5 + 3H_2O$; the assumption that it is the pentasulphide which is produced is arbitrary. The first part of this reaction between sulphide and sulphite becomes clearer if the hydrion concentration is considered; then the formation of thiosulphate proceeds thus: $2NaSH + 4NaHSO_3 \longrightarrow 3Na_2S_2O_3 + 3H_2O$. The mixture of Na_2S_5 and $Na_2S_2O_3$ obtained by dry heating is the principal constituent of "liver of sulphur." The reaction between caustic soda and sulphur is a kind of hydrolysis, and may be compared with its action on chlorine giving NaCl and NaClO, and on phosphorus giving PH_3 and NaH_2PO_2.

Thiosulphates are produced by the oxidation of polysulphides; sulphites are formed as intermediate products: $Na_2S_5 + 3O \longrightarrow Na_2SO_3 + 4S$. Polysulphides are thus converted into thiosulphates by exposure to the air. When the former are heated with water, even out of contact with air, thiosulphates are again formed. Alkali hydroxide and H_2S_x are first formed by hydrolysis; the latter decomposes, and the liberated sulphur then reacts with the hydroxide to give thiosulphate in the manner already described. The sodium salt is obtained by the action of iodine on a mixture of sulphite and sulphide. The sulphur set free by the reaction $Na_2S + I_2 \longrightarrow 2NaI + S$ unites with the sulphite. Thiosulphates are also made by the action of alkalis, alkali sulphides or cyanides on polythionates (see p. 565). The mechanism of this process is rather obscure, but probably depends upon the formation of sulphite and sulphur; Na_2S may replace alkali in this reaction, its hydrolysis with water supplying the necessary NaOH.

It is stated that sulphites can take up selenium, giving derivatives of the acid H_2SSeO_3.

The structure of the thiosulphates has not been definitely established.

Werner regards them as compounds intermediate between the sulphates and pentasulphides:

$$\left[SO_4 \right] M_2 \qquad \left[S^{}_{} {\textstyle {S \atop O_3}} \right] M_2 \qquad \left[S(S_4) \right] M_2.$$
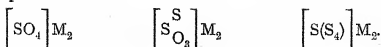
Objections to this view are the non-existence of salts of the type $\left[S {\textstyle {S_2 \atop O_2}} \right] M_2$, and the general properties of pentasulphides. These compounds are not the final members of the polysulphide series (*cf.* p. 539 *et seq.*), and probably have a different structure from the one given above. The fundamental reaction of iodimetry, viz. the formation of sodium tetrathionate from iodine and thiosulphate, is expressed:

$$\text{NaO.SO}_2.\text{S} \boxed{\text{Na} + \text{I} \,|\, \text{I} + \text{Na}} \text{S.SO}_2.\text{ONa} \longrightarrow 2\text{NaI} + \text{NaO.SO}_2.\text{S.S.SO}_2.\text{ONa},$$
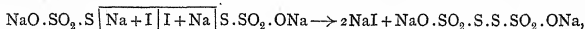
but as this most probably is not the structure of tetrathionate (see p. 560), the equation is no proof that thiosulphate has the constitution

$$SO_2 \begin{smallmatrix} \diagup \text{SNa} \\ \diagdown \text{ONa} \end{smallmatrix} \qquad .$$ Claims for $$\begin{smallmatrix} O \searrow \\ S \diagup \\ S \nearrow \end{smallmatrix} S \begin{smallmatrix} \diagup \text{ONa} \\ \diagdown \text{ONa} \end{smallmatrix}$$ might also be put forward.
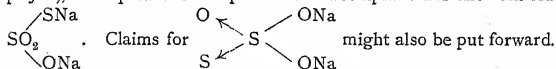
This sulphur atom is only weakly attached to the sulphite molecule; many thiosulphates are not stable even at ordinary temperatures; the free acid has not been isolated, as it decomposes rapidly into sulphurous acid and sulphur. Thiosulphates are decomposed by acids with evolution of sulphur dioxide and the formation of a precipitate of sulphur, and hence acid salts cannot be prepared. It is some time before any turbidity appears. The delay may be caused by the formation of a colloidal solution of sulphur which gradually coagulates, and not to the thiosulphuric acid decomposing slowly. This is experimentally verified by neutralising the liquid with alkali as soon as the acid has been added. The formation of the sulphur precipitate is not prevented, but it may not have proceeded quantitatively. The solution remains clear for a longer time if alcohol is added, because the sulphur sol is more stable in alcoholic than in aqueous solution. Gil and Beato[1] obtained dilute solutions of thiosulphuric acid, stable for several days, either by decomposing lead thiosulphate, suspended in alcohol, by H_2S, or by adding a little concentrated sodium thiosulphate solution to cool, fuming, hydrochloric acid. It must also be observed that the decomposition of thiosulphuric acid does not proceed according to the simple equation $H_2S_2O_3 \longrightarrow H_2SO_3 + S$, for appreciable quantities of polythionates are also formed.

Bassett and Durrant[2] consider that the decomposition may take place in at least 3 ways, represented by the reversible reactions:

(1) $H_2S_2O_3 \rightleftharpoons H_2SO_3 + S$
(2) $2H_2S_2O_3 \rightleftharpoons H_2S + H_2S_3O_6$
(3) $2H_2S_2O_3 \rightleftharpoons H_2O + H_2S_4O_5.$
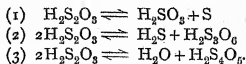
[1] *Ber.*, 1923, 56B, 2451.   [2] *J. Chem. Soc.*, 1927, 1416.

(1) is usually the predominant reaction, and is bimolecular, so that the mechanism is possibly $2H_2S_2O_3 \rightleftharpoons 2H_2SO_3 + S_2$. With regard to (2), it has long been known that H_2S is evolved from acidified solutions of thiosulphates, especially if the solutions are strongly acidified. Trithionates are invariably formed during such decompositions, and being the least stable of the polythionates, then undergo further change. Reaction (3) occurs chiefly in very strongly acidic solutions, dithiopyrosulphuric acid, $H_2S_4O_5$, resulting, for no sulphur is precipitated, and even after fifteen hours the solution remains clear. Kurtenacker and Czernotzky[1] suggest, however, that in stage (3) the compound is $H_2S_2O_3 . SO_2$, for if SO_2 is passed into a thiosulphate solution, it becomes yellow and then colourless. Addition of sodium hydroxide produces sulphite and thiosulphate, but sulphur is not precipitated; with formaldehyde and NaOH, which presumably will react with SO_2 to form sodium formaldehyde bisulphite, sulphur is precipitated owing to decomposition of the thiosulphate, but no polythionate is present.

The reaction with formaldehyde is also used, for example, in determining thiosulphate in presence of sulphite, for the former is unaffected and can be titrated by iodine in the usual way; the latter, on account of its conversion to sodium formaldehyde bisulphite, is rendered inactive.

The thiosulphates of metals which give insoluble sulphides are extremely unstable. Salts of metals which can be precipitated by H_2S from acid solution give transient bright-coloured precipitates with sodium thiosulphate, which change almost instantly into the dark sulphides. The colour gradation with mercuric, silver and lead salts is striking; the white precipitates which are first formed quickly become yellow, then brown and finally black. These changes take place still more rapidly when the solutions are warmed. If, however, an excess of mercuric salt is used, a perfectly stable white precipitate, $HgCl_2 . 2HgS$, is obtained and by titrating the acid formed, this reaction can be used for the estimation of thiosulphate:

$$2Na_2S_2O_3 + 3HgCl_2 + 2H_2O \longrightarrow 2Na_2SO_4 + 4HCl + HgCl_2 . 2HgS.$$
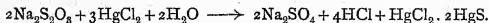
The thiosulphates of heavy metals decompose into sulphides both in the dry state and when heated with water. Solutions of the salts of Al, Cr, Ti, Th and Zr give precipitates of hydroxides owing to hydrolysis of the sulphides; the hydroxides are often granular and consequently such precipitations are applied in gravimetric analysis. Thiosulphates of the alkali, alkaline earth and ammonium sulphide analytical group of metals belong to the soluble, stable type. Sulphides of the ammonium sulphide group are precipitated when the solutions are acidified. The majority of the solid thiosulphates contain water of crystallisation; only the most insoluble, e.g. the lead salt, are

[1] Z. anorg. Chem., 1928, 175, 231.

anhydrous. The thiosulphates are very unstable when dry. Dry calcium thiosulphate sometimes decomposes violently, and becomes a yellow, pasty mass. The solid alkali salts are very stable, especially if they are not exposed to the air. In solution they decompose only very slowly, but solutions used for volumetric analysis must be restandardised at intervals.

Thiosulphates are oxidised to tetrathionates by mild oxidising agents. The action with iodine has been described. Ferric and cupric salts, PbO_2, Na_2O_2, SeO_2 and persulphates can also be employed:

$$2Na_2S_2O_3 + 2FeCl_3 \longrightarrow 2NaCl + 2FeCl_2 + Na_2S_4O_6.$$
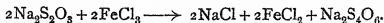
Small quantities of sulphuric acid are produced during this reaction. Polythionic acids are also obtained by the action of hydrogen peroxide, but stronger reagents, such as chlorine and bromine, oxidise thiosulphates to sulphuric acid; it has been shown that polythionic acids are formed as intermediate products. Tetrathionates are obtained by electrolytic oxidation in neutral solution: $2S_2O_3'' \longrightarrow S_4O_6''$; the process is not primarily one of anodic condensation, for the presence of H_2O_2 formed during the electrolysis is essential to the change.[1] The reaction with sulphurous acid yields a complicated mixture of polythionates and forms a strong contrast to the simple oxidation by iodine; sulphur monochloride and potassium thiosulphate yield tetrathionate as the highest polythionate. From a concentrated solution of potassium thiosulphate and sulphurous acid, trithionate is the main product $(2K_2S_2O_3 + 3SO_2 \longrightarrow 2K_2S_3O_6 + S)$, but higher polythionates and less free sulphur may be formed, for example:

$$6K_2S_2O_3 + 9SO_2 \longrightarrow K_2S_5O_6 + K_2S_4O_6 + 4K_2S_3O_6.$$
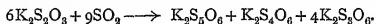
When heated dry, solid thiosulphates decompose into sulphates and polysulphides; the latter lose part of their sulphur at a high temperature. This oxidation-reduction is characteristic of salts of an intermediate state of oxidation. The action of water is similar: $H_2S_2O_3 + H_2O \longrightarrow H_2SO_4 + H_2S$. This hydrolysis takes place in the cold in the presence of ions of heavy metals, and is the cause of the precipitation of the metallic sulphides by thiosulphates.

The soluble salts of thiosulphuric acid contain water of crystallisation; the almost insoluble barium salt is anhydrous at room temperature. The alkali salts can be desiccated without decomposition, but sulphur is readily lost at a high temperature. Many thiosulphates are unaffected by the air; lithium thiosulphate is deliquescent, as also the zinc salt, which has not been isolated in the dry state. Salts which contain much water of crystallisation are also unstable, e.g. the hexahydrate of calcium thiosulphate and the well-known sodium salt, which crystallises with 5 mols. of water in large transparent prisms.

[1] Glasstone and Hickling, *J. Chem. Soc.*, 1932, 2345, 2800.

Lower hydrates of sodium thiosulphate are known. The transition point of the pentahydrate and the anhydrous salt is 48·4°; this temperature is also the melting point of the pentahydrate. This salt affords an excellent example of undercooling and is often used for demonstration. If a crystal of thiosulphate is dropped into the undercooled liquid, the whole mass solidifies instantly, with evolution of heat.

Some of the more important hydrated thiosulphates are :

Thiosulphate of	Ba	K	Cd	Li	Sr, Mn, Na	Ca, Mg, Ni, Co
Mols. H_2O	1	$\frac{3}{2}$	2	3	5	6

The solubility of sodium thiosulphate per 100 parts of water is :

Temperature	0°	20°	45°	50°	80°
	33.4	41·2	55·3 (parts penta-hydrate)	67·8	69·9 (parts anhyd. salt)

The solubility of the hydrate thus increases rapidly with rise of temperature ; that of the anhydrous salt remains nearly constant. Lithium and zinc thiosulphates dissolve in alcohol. At·3° the calcium salt is soluble in its own weight of water, the strontium salt dissolves in 4 parts of water at 13°, and in 1·75 parts at 100°.

Complex Salts.—Thiosulphates which are insoluble in water dissolve in excess of alkali thiosulphate solution ; the formation of very stable complex salts is indicated by the fact that the metals in them are not precipitated by the usual reagents. Silver, mercuric and cuprous iodides and lead sulphate are soluble in sodium thiosulphate. If an excess of thiosulphate is added to a silver solution, the metal is not precipitated by soluble iodides. Some of these complex salts have simple formulae, but others are very complicated. The simpler salts include

$$M[Ag(S_2O_3)] \qquad M_2[Hg(S_2O_3)_2] \qquad M_3[Bi(S_2O_3)_3]$$
i.e. $Ag_2S_2O_3 . M_2S_2O_3 \qquad HgS_2O_3 . M_2S_2O_3 \qquad Bi_2(S_2O_3)_3 . 3M_2S_2O_3 .$
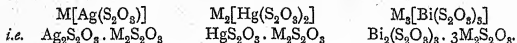
Bassett and Lemon[1] identified the following compounds from a phase-rule study :

$$Na[Ag(S_2O_3)H_2O] \qquad Na[Ag_3(S_2O_3)_2]H_2O$$
$$Na_3[Ag(S_2O_3)_2]2H_2O \qquad Na_5[Ag_3(S_2O_3)_4]2H_2O.$$

They consider that each contains the anion
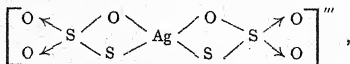
e.g. $Na'_3[Na_2(H_2O)_2]''Ag'[(S_2O_3)Ag(S_2O_3)]_2'''.$ Other derivatives are given by cadmium, arsenic, antimony, etc. The following copper and silver salts may be cited as examples of complicated compounds, *e.g.* $4Cu_2S_2O_3 . 3Na_2S_2O_3 . 6H_2O$; $5Cu_2S_2O_3 . 4Na_2S_2O_3 . 8H_2O$; $3Ag_2S_2O_3 . 5K_2S_2O_3$, etc. The constitution of many of these salts, *e.g.* $HgS_2O_3 . 4M_2S_2O_3$, is not yet clear. The acid $H[Ag(S_2O_3)]H_2O$ has been prepared. A large number of these complex salts possess a

sweet taste; the silver salt $Na[Ag(S_2O_3)]$ diluted to one part in 320,000 still tastes distinctly sweet. The thiosulphates of the heavy metals also form ammines with ammonia.

Dithionic Acid, $H_2S_2O_6$.—This acid has the constitution $HO_3S.SO_3H$, with two sulphur atoms directly linked together; this view is confirmed by a study of the X-ray structure,[1] leading to the formulation

of the ion, $\begin{bmatrix} O & & & O \\ O & \leftarrow S - S \rightarrow & O \\ O & & & O \end{bmatrix}''$ and showing its relation to the structure

of the pyrosulphite ion,[2] $\begin{bmatrix} O & & & O \\ O & \leftarrow S - S & & \\ O & & & O \end{bmatrix}'$ derived from the X-ray

analysis of $Na_2S_2O_5$. For a general discussion of the S—O bond see p. 575.

Bassett and Henry [3] made a careful study of conditions of formation of dithionate and showed that it results from oxidation of pyrosulphite. It is prepared practically by the oxidation of sulphurous acid: $2SO_3H \longrightarrow H_2S_2O_6$. Rapid oxidation must be avoided or sulphuric acid is formed; traces of this acid are obtained even when the oxidation is carried out slowly. Oxidising agents which can be suspended in water are very suitable; chemical action is then confined to the surface layers. Suspensions of manganese dioxide, ferric and cobaltic hydroxide, etc., give good yields of dithionic acid. Barium peroxide must not be employed, because the H_2O_2 produced by the action of water oxidises the lower acid to sulphuric acid. Persulphuric acid can, however, be used as an oxidising agent, although some H_2O_2 is formed during the reaction. Dithionates are also prepared by the electrolytic oxidation of neutral or alkaline solutions of sulphites. By this process the dithionates are derived from SO_3'' ions and not from HSO_3' ions; therefore free acid must not be present. If a solution of free dithionic acid is concentrated till the density becomes 1·347, it decomposes into H_2SO_4 and SO_2, though the acid has not yet been obtained by the reverse reaction: $H_2SO_4 + SO_3 \longrightarrow H_2S_2O_6$. On dry heating, the salts also give off SO_2 and leave a residue of sulphate.

Dithionic acid, unlike the higher members of the series, is remarkably stable towards oxidising agents. It is not attacked in the cold by chlorine water or nitric acid; nor will it unite with sulphur like trithionic and tetrathionic acids. Probably dithionic acid has a structure different from that of the higher polythionic acids (cf. p. 560

[1] Helwig, Z. Krist., 1932, 83, 485.
[2] Zachariasen, Physical Rev., 1932, 40, 923,
[3] J. Chem. Soc., 1935, 914,

et seq.). It is not formed by methods which give mixtures of the higher acids, and the stability of its alkali and alkaline earth salts in solution is very marked; such solutions can be boiled without decomposition. The salts of the heavy metals are less stable, probably owing to hydrolysis, with liberation of free dithionic acid. The anhydrous alkali salts lose SO_2 at a definite dissociation temperature thus[1]: $M_2S_2O_6 \longrightarrow M_2SO_4 + SO_2$.

The dithionates are all soluble in water, in which respect they resemble the nitrates and chlorates, which have similar formulae:

$$MNO_3 \qquad MClO_3 \qquad (MSO_3)_2.$$
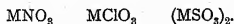
The potassium salt is relatively insoluble, one part dissolving in 16.5 parts of water at room temperature; the barium and lead salts are soluble in their own weight of water at the boiling point. The crystalline hydrates have the following compositions:

> Anhydrous: K, Rb, Tl salts.
> With $2H_2O$: Na, Li, Ag, Ba salts.
> With $4H_2O$: Ca, Sr, Pb salts.
> With $6H_2O$: Mg, Mn, Ni, Zn, Cd salts.

Thus the alkali salts contain the least water of crystallisation, resembling in this the alkali chlorates and nitrates. Acid dithionates are unknown; but it would be incorrect to assume that the acid should be represented by the halved formula. Measurements of the conductivity of sodium dithionate prove conclusively that the acid is dibasic.

Higher Polythionic Acids. Tri-, Tetra-, Penta- and Hexa-thionic Acids.—$H_2S_3O_6$, $H_2S_4O_6$, $H_2S_5O_6$ and $H_2S_6O_6$.

These compounds are sometimes formulated with chains of the general type: $HO.SO_2.S_{x-2}SO_2OH$, *e.g.*

$$HO_3S.S.SO_3H \qquad\qquad HO_3S.S.S.S.SO_3H$$
Trithionic acid.   Pentathionic acid.

The structures are not, however, supported by the interrelations of the acids. The members of the series are readily converted into one another, and it is improbable that a chain of atoms would easily break up in order to expel or admit a single sulphur atom. Bassett and Durrant consider that tetrathionates probably consist of two forms in equilibrium, namely:

HO——S——S——S——OH and HO——S——S——S——S——OH.
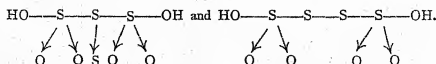
The decomposition of the higher polyacids results in the formation of trithionic acid; dithionic acid is never produced. The chain theory does not explain why the decomposition is arrested at the trithionic stage. Similarly tri- and

[1] Tammann and Boehme, *Z. anorg. Chem.*, 1932, **204**, 143.

tetra-thionic acids, but not dithionic acid, can be converted into the higher members. Further, the higher polythionic acids are easily oxidised to sulphuric acid, but dithionic acid is oxidised only with great difficulty. It has also been suggested that these compounds resemble polysulphides, and that the higher members are derived from one parent acid. The mobility of the sulphur atoms is evidence for such a structure. Obviously the parent acid would be trithionic acid. Assuming the truth of the hypothesis, the production of the higher members may be represented thus :

$$H_2S_3O_6 + xS \rightleftharpoons H_2S_{3+x}O_6.$$
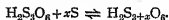
Trithionic acid is thus formulated

$$HO—S—S—S—OH$$

and this formula is supported
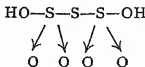
by the results of X-ray analysis[1]; the valency angle for the central sulphur atom is 103°. The other acids are variously represented, but in general they are regarded as derivatives of trithionic acid, such as
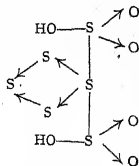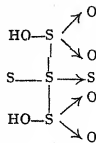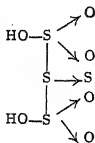
For a general discussion of the S—O bond, see p. 575.

The constitution, formation and decomposition of the polythionic acids are much more complicated than had previously been supposed (see, for example, F. Förster; Riesenfeld; Raschig and Kurtenacker[2]; Vogel[3]; Bassett and Durrant[4]).

Polythionic acids are invariably produced when sulphurous acid comes into contact with finely divided sulphur.[5] In general, a mixture of acids is obtained, but one compound is often present in predominant quantity. The polythionic acids are most conveniently obtained by the action of nascent sulphur on H_2SO_3. Three important methods are used:

1. The decomposition of thiosulphates by acids in the presence of an arsenite; an almost theoretical yield of polyacids is obtained by this process. Pentathionic acid is formed in largest quantity.[6] In the absence of arsenites the sulphur liberated by the decomposition $H_2S_2O_3 \longrightarrow H_2SO_3 + S$ is almost entirely precipitated, and only traces of polythionic acids are produced (cf. p. 555). The best results are obtained when the thiosulphate is decomposed with sulphuric acid or

[1] Zachariasen, J. Chem. Physics, 1934, 2, 109.
[2] Z. anorg. Chem., 1923, 126-132.   [3] J. Chem. Soc., 1925, 127, 2248.
[4] J. Chem. Soc., 1927, 1401.   [5] Debus, Ann., 1888, 244, 76.
[6] Raschig, Z. angew. Chem., 1920, 33, 260.

bisulphites; in the absence of arsenite, pentathionic acid is first formed, and then gives the other thionic acids, thus:

$$5H_2S_5O_6 \longrightarrow 2H_2S_5O_6 + 3H_2O$$
$$2H_2S_5O_6 + 3H_2SO_3 \longrightarrow H_2S_6O_6 + H_2S_4O_6 + 3H_2S_2O_3.$$
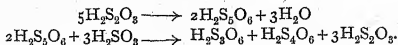
2. Sulphuretted hydrogen is passed through an excess of a cold aqueous solution of sulphur dioxide. Under these conditions the familiar reaction: $SO_2 + 2H_2S \longrightarrow 2H_2O + 3S$ is accompanied by others. A considerable portion of the liberated sulphur, probably while in the nascent state, is absorbed by sulphurous acid with the formation of polythionic acids. The reaction is a very slow one, and in practice small quantities of H_2S are bubbled through the liquid at intervals of several days. The milky liquid finally obtained is called *Wackenroder's solution*; it contains tetrathionic and pentathionic acids, traces of trithionic and sulphuric acids, but no dithionic acid. The quantity of tetrathionic acid is independent of the time allowed for the reaction; the higher acids, however, are formed in larger quantity when the process is carried out more slowly. These acids might be derived from the lower members of the series, but recent work shows that pentathionic acid is the primary product, which, by its reaction with sulphurous acid, gives other thio-acids and sulphur, the latter forming thiosulphuric acid, with further reaction as above.

According to Riesenfeld and Feld,[1] SO is the first product of the reaction between H_2S and SO_2 (for SO see p. 544). Thiosulphuric and pentathionic acids are then formed by the hydrolysis of the SO: $H_2O + 2SO \longrightarrow H_2S_2O_3$; $H_2O + 5SO \longrightarrow H_2S_5O_6$; the oxidation of SO in presence of excess of SO_2 gives $H_2S_2O_4$ and $H_2S_2O_3$. Thiosulphates are momentarily formed in neutral or alkaline solution. Bassett and Durrant consider that trithionic acid is the primary thionic acid formed in the Wackenroder reaction, and that by such reactions as $H_2S_2O_6 + S \rightleftharpoons H_2S_4O_6, H_2S_4O_6 + S \rightleftharpoons H_2S_5O_6, H_2S_3O_6 + H_2S_2O_3 \rightleftharpoons H_2S_4O_6 + H_2SO_3$; and $H_2S_4O_6 + H_2S_2O_3 \rightleftharpoons H_2S_5O_6 + H_2SO_3$, the other thionic acids are formed.

F. Förster,[2] for reasons not easy to give in brief, suggests that sulphoxylic acid is an intermediate product in the formation of polythionates. The pentathionic acid is then produced as follows:

$$H_2S + H_2SO_3 \rightleftharpoons H_2S_2O_2 + H_2O$$
$$H_2S_2O_2 + H_2SO_4 + H_2O \longrightarrow 3H_2SO_2$$
$$2H_2SO_2 \longrightarrow H_2S_2O_3 + H_2O$$
$$5H_2S_2O_3 \rightleftharpoons 2H_2S_5O_6 + 3H_2O.$$
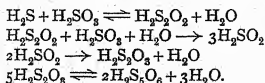
3. Sulphurous acid and sulphur are produced simultaneously by the action of water upon sulphur chloride; as might be expected, small quantities of polythionic acids are also found among the products.

[1] *Z. anorg. Chem.*, 1921, 119, 225.   [2] *Ber.*, 1924, 57, 258.

The yield of these acids is increased by carrying out the action in the presence of excess of sulphurous acid.

The preparation of tetrathionic acid is dealt with on p. 557.

Trithionates can best be prepared by the oxidation of thiosulphates with sulphur dioxide (see p. 557) or with hydrogen peroxide:

$$2Na_2S_2O_3 + 4H_2O_2 \longrightarrow Na_2S_3O_6 + Na_2SO_4 + 4H_2O.$$
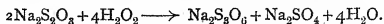
In this reaction tetrathionates are the first products:

$$2Na_2S_2O_3 + H_2O_2 \longrightarrow 2NaOH + Na_2S_4O_6,$$
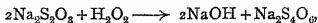
but the sodium hydroxide formed removes sulphur from the tetra-thionate, leaving the trithionate.[1]

Hexathionic acid is also formed by the oxidation of thiosulphates. The existence of this acid, originally mentioned by Debus, was considered doubtful for some time, but E. Weitz and F. Achterberg[2] have re-established it. The potassium salt is formed by oxidising thio-sulphate (3 mols.) with nitrite (1 mol.) in presence of well-cooled hydrochloric acid, a reaction which gives varied colours in solution, due in all probability to the formation of nitrosyl thiosulphuric acid, $HO_3S.S.NO$.

The free polythionic acids are known only in solution. Pentathionic acid has been stated to be the most stable of the series; its solution can be concentrated without decomposition until the density reaches 1·5, but tetrathionic acid is also described as the most stable acid. The acids are obtained by decomposing solutions of the potassium salts with perchloric acid, or the lead or barium salts with sulphuric acid. The solutions of the polythionic acids are rendered more stable by the addition of a little mineral acid; they decompose quickly in the presence of free alkali. The salts crystallise more easily from slightly acid solutions. The potassium salts are the best known. They are prepared by the action of potassium acetate on the solution of the polythionic acid in the presence of a little free acid; the liquid is then evaporated and the salt recrystallised from acidified water. The acetate is employed in the preparation in order to prevent too great a concentration of $H^{\cdot}$ ions being formed during the reactions. Solutions of the free polythionic acids slowly decompose. Trithionic acid breaks up according to the equation $H_2S_3O_6 \longrightarrow H_2SO_4 + SO_2 + S$.

Some of the sulphur, however, is absorbed by unchanged trithionic acid with the production of higher acids; these in turn decompose, and the lower acids are constantly re-formed with separation of sulphur. A solution of hexathionic acid is therefore soon found to contain pentathionic acid, and tetrathionic acid is quickly formed in a solution of pentathionic acid. Tetrathionic acid decomposes into tri- and penta-

[1] Raschig, *Schwefel- und Stickstoffstudien*, p. 284.
[2] *Ber.*, 1928, 61, 399.

thionic acids. A solution of any polythionic acid is ultimately converted into a mixture of all the acids, but in each case the final products are sulphuric acid, sulphur dioxide and sulphur.

The polythionic acids are dibasic, although acid salts are unknown. The potassium salts have been examined the most thoroughly; these compounds, including the dithionate, are well crystallised. The polythionates are all easily soluble in water except the salts of silver and mercury, which, however, cannot be precipitated without decomposition. Mercuric chloride reacts with all polythionates as follows :

$$2Na_2S_{2+x}O_6 + 3HgCl_2 + 4H_2O \longrightarrow HgCl_2 . 2HgS + 2xS + 4NaCl + 4H_2SO_4.$$
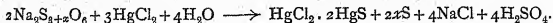
The increase in acidity, therefore, gives a measure of the total polythionate present.[1] Tetrathionates are precipitated from solution by the addition of alcohol, and solutions of the alkali salts are stable. The polythionates of the alkaline earth metals are less stable, and those of the heavy metals are very unstable; e.g. CuS is gradually precipitated from a solution of copper tetrathionate. Many polythionates of the heavy metals can be obtained in the crystalline state, but they are not precipitated by adding alkali polythionates to solutions containing heavy metals. Copper trithionate is instantly decomposed by copper sulphate, copper sulphide being precipitated. This reaction, which is peculiar to copper trithionate, can be used for the estimation of trithionic acid in the presence of other polythionates :

$$S_3O_6'' + Cu^{..} + 2H_2O \longrightarrow CuS + 2SO_4'' + 4H^..$$

Riesenfeld and Sydow [2] found that, if a mixture of trithionate $CuSO_4$, $BaCl_2$ and HCl is boiled, the reaction proceeds quantitatively as follows :

$$S_3O_6'' + 8Cu^{..} + 6H_2O = 3SO_4'' + 8Cu^. + 12H^..$$
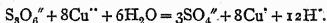
Potassium trithionate is separated from tetra- and pentathionates by fractional crystallisation of the mixture obtained from Wackenroder's solution, for the trithionate is more soluble than the other salts. The solubilities of potassium tetrathionate and pentathionate are almost identical. These salts are separated from each other by levigation, by sorting the crystals by hand, or by using a mixture (sp. gr. 2·2) of bromoform and xylene in which potassium tetrathionate sinks and the pentathionate floats.

The polythionates form sulphates on oxidation. Tetrathionates are converted back into thiosulphates by the action of reducing agents. Many of the reactions undergone by polythionates involve the loss of sulphur. Tetrathionate and free sulphur are formed at once by the

[1] For estimation of the various sulphur acids in admixture see Mitchell and Ward, *Modern Methods in Quantitative Chemical Analysis*, Longmans, 1932.
[2] *Z. anorg. Chem.*, 1928, 175, 74.

action of caustic potash on the pentathionate; the tetrathionate is more resistant to the action of this reagent and can thus be isolated from the mixture of thio-acids and free sulphur. The polythionates are, however, all converted into thiosulphates when boiled with caustic alkalis:

$$2K_2S_5O_6 + 6KOH \longrightarrow 5K_2S_2O_3 + 3H_2O,$$
$$2K_2S_4O_6 + 6KOH \longrightarrow 3K_2S_2O_3 + 2K_2SO_3 + 3H_2O,$$
$$2K_2S_3O_6 + 6KOH \longrightarrow K_2S_2O_3 + 4K_2SO_3 + 3H_2O.$$
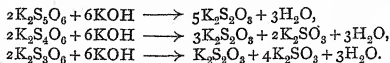
Thiosulphates are also formed by the action of potassium sulphide on the trithionate: $K_2S_3O_6 + K_2S \longrightarrow 2K_2S_2O_3$. With tetra- and pentathionates the reaction is similar, thiosulphate and sulphur being formed:

$$K_2S_{3+x}O_6 + K_2S \longrightarrow 2K_2S_2O_3 + xS.$$

The reactions with sodium sulphite are interesting and support the view that the higher polythionic acids are derived from trithionic acid; the pentathionates and tetrathionates are converted into the trithionate which is itself unattacked by the sulphite:

$$Na_2S_4O_6 + Na_2SO_3 \longrightarrow Na_2S_3O_6 + Na_2S_2O_3,$$
$$Na_2S_5O_6 + 2Na_2SO_3 \longrightarrow Na_2S_3O_6 + 2Na_2S_2O_3.$$
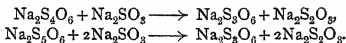
The total quantity of higher salts present in a mixture of polythionates can be ascertained with the aid of a volumetric determination of the excess sulphite by iodine.

The polythionates react with potassium cyanide as follows:

$$K_2S_3O_6 + 2KCN + H_2O \longrightarrow K_2SO_4 + 2HCN + K_2S_2O_3.$$
$$K_2S_4O_6 + 3KCN + H_2O \longrightarrow K_2SO_4 + 2HCN + K_2S_2O_3 + KCNS.$$
$$K_2S_5O_6 + 4KCN + H_2O \longrightarrow K_2SO_4 + 2HCN + K_2S_2O_3 + 2KCNS.$$
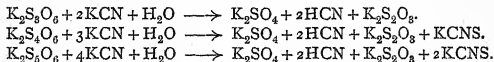
The *hexathionates* have not yet been investigated in detail, but their general reactions are similar to those of the pentathionates, *e.g.* the removal of sulphur by alkalis, the formation of yellow precipitates with mercurous and mercuric salts, and of brown colorations, with subsequent precipitation of sulphide, with silver nitrate. They differ from trithionates in giving no precipitate with copper sulphate, and from pentathionates by the less rapid separation of sulphur on addition of alkali. Hexathionates are converted into trithionates by alkali sulphites; they give characteristic precipitates with luteo-cobalt and chromium salts, as also with benzidine, though other polythionates also give precipitates with the last.

Polythionic acids in which part of the sulphur has been replaced by selenium appear to exist.

Sulphur Trioxide, SO_3.—This oxide can be obtained by dehydration of sulphuric acid with phosphorus pentoxide. Although concentrated sulphuric acid invariably contains traces of SO_3, and decomposes at a

high temperature into SO_3 and H_2O, the trioxide cannot be isolated
from this mixture, as both products of the decomposition are equally
volatile at this temperature and recombine on condensation. Sulphur
trioxide can, however, be obtained by heating compounds in which
the anhydride is combined with non-volatile components; the sulphates
of feebly basic metals are suitable; e.g. ferric sulphate is decomposed
by heat into SO_3 and a residue of oxide: $Fe_2(SO_4)_3 \longrightarrow Fe_2O_3 + 3SO_3$.

Formerly a basic ferric sulphate was made by the exposure of pyrites (FeS_2) or
ferrous sulphate to damp air; the residue of Fe_2O_3 (caput mortuum) left by ignition
of these sulphates varies in colour from a bright yellow to a reddish purple, and is
used as a pigment.

The sulphates of strongly electropositive metals are decomposed
by heat with the greatest difficulty, but the sulphur trioxide is expelled
by heating the sulphate with a relatively non-volatile acid anhydride.
A small quantity of SO_3 is displaced from combination, and, being
volatile, escapes from the system. The process continues until the
whole of the SO_3 has been replaced by the second anhydride. Silica
in the form of quartz or sand is generally used as the non-volatile acid
anhydride. The reaction with gypsum is expressed by the equation
$CaSO_4 + SiO_2 \longrightarrow CaSiO_3 + SO_3$. The magnesium sulphate left as a
by-product in the industrial extraction of potash salts is also decomposed
by sand; as magnesium is less electropositive than calcium, the SO_3
is given off at a lower temperature.

The pyrosulphates are decomposed by heat with the formation of
sulphates and evolution of SO_3: $K_2S_2O_7 \longrightarrow K_2SO_4 + SO_3$. Pyro-
sulphuric acid undergoes the same change when gently warmed:
$H_2S_2O_7 \longrightarrow H_2SO_4 + SO_3$; this is a convenient method of preparation
in the laboratory, but since the formation of pyrosulphuric acid involves
the use of sulphur trioxide, these methods can only be applied to
the preparation of small quantities of the anhydride.

The most important method is by the synthesis: $2SO_2 + O_2 \longrightarrow 2SO_3$.
This reaction is exothermic and liberates 45·2 Cals.; it might be
expected to proceed to completion at the normal temperature, but the
rate of combination then becomes imperceptible. When sulphur is
burned in an excess of oxygen, only small traces of SO_3 are formed;
this is because the trioxide is very unstable at the temperature of
burning sulphur and decomposes according to the reverse reaction.
The maximum combination of SO_2 and O_2 occurs at 400° in the
presence of a contact catalyst; the yield of SO_3 under industrial
conditions becomes negligible at a temperature above 950° or
below 200°.

The synthetic production of sulphur trioxide, now of such importance in the
manufacture of sulphuric acid, was discovered by Davy and made the subject of a
patent by Phillips in 1831 (English Pat. 6096). At first the method was not a success
on the large scale because the catalyst was soon poisoned and its activity destroyed.

Many of the practical difficulties were removed by the researches of Winkler,[1] and finally the Badische Anilin- und Sodafabrik, under the management of Knietsch, made the contact process a commercial success.[2]

Platinised asbestos is a very efficient catalyst. It is assumed[3] that an endothermic peroxide of platinum is first formed which then oxidises the SO_2. Metallic oxides which are susceptible to alternate oxidation and reduction—e.g. Fe_2O_3 (burnt pyrites) and V_2O_5—are used instead of platinum. The SO_2, obtained by roasting pyrites, is mixed with air and passed over the catalyst. The equilibrium constant for the reaction is $K = \dfrac{(SO_2)^2 \times (O_2)}{(SO_3)^2}$; it is clear from this expression that the yield of SO_3 will become larger as the proportion of oxygen in the mixture is increased. An excess of air is therefore employed, and very dilute mixtures of SO_2 can be worked up.

The following values for log K are obtained:

Temperature	528°	627°	727°	832°	897°
Log K	− 4·81	− 3·50	− 2·45	− 1·55	− 1·09

A furnace gas of composition 7 per cent. SO_2, 10 per cent. O_2 and 83 per cent. N_2, gave the following yields of SO_3:

Per cent. SO_3	96	80	58	35	15	0
Temperature	500°	600°	700°	800°	900°	1000°

The gas, as it comes from the pyrites burners, must be thoroughly purified before it is allowed to enter the contact chamber. The particles of dust, which are plainly visible in the gas, would quickly poison the catalyst, and are first removed by a mechanical process. Another objectionable impurity is finely divided sulphur, which is eliminated by injections of steam through the hot gases ; a very large excess of air is unable to remove the whole of the sulphur without the use of steam. There still remain traces of other impurities, mercury, arsenic and phosphorus, which are derived from the pyrites and are particularly harmful to the catalyst ; if present to the extent of only 1·2 per cent. in it the catalyst is completely poisoned. The activity of the catalyst is easily impaired, for in the course of a few months enormous quantities of gas pass through a very small amount of platinised asbestos. The gas can, however, be obtained perfectly pure if it is thoroughly washed and then filtered while still damp. Even the slight traces of arsenic which are absorbed by the gaseous mixture, probably as AsH_3, from the iron while being conducted through the cooling pipes, are removed. The sulphuric acid, of which a small quantity is formed before the gases enter the contact chamber, is not allowed to come in contact with iron piping. A 98-99 per cent. yield of SO_3 is obtained if the process is carried out with the full precautions described.

Since heat is generated by the oxidation of sulphur dioxide, the catalyst tends to get hotter during the working of the plant. Such superheating reduces the efficiency of the catalyst. The rise of temperature is therefore prevented by cooling the contact apparatus by means of the gaseous mixture before it is submitted to the catalytic action ; and this method has the additional advantage that the gases are at the same time heated to the requisite temperature, with a consequent saving in fuel. The catalyst is contained in cylinders, which are slightly heated at the end at which the gases enter the contact chamber.

The absorption of the SO_3 by water presents great difficulty, because the trioxide has a strong tendency to remain in the form of a fog. In spite of the very hygroscopic nature of solid SO_3, the gas which leaves the contact chamber can be passed through

[1] D.R.P., 1878, 4566.   [2] Ber., 1901, 34, 4069.
[3] Wöhler, Foss and Plüddemann, Ber., 1906, 39, 3538.

many receivers of water without being completely absorbed. The affinity of SO_3 for sulphuric acid, which reaches a maximum when the concentration of the acid is 98.3 per cent., is utilised to effect the absorption. The fumes are therefore passed into acid of this strength, and the concentration is maintained constant by a stream of water which flows simultaneously into the condensing tank.

Properties.—Sulphur trioxide has long been supposed to exist in two monotropic forms. The α-variety is produced only by the condensation of the vapour. It is a colourless liquid, which may easily be undercooled, and crystallises in long transparent prisms, m.pt. 17.1°; b.pt. 46.2°. On standing, the α-form gradually changes into the β-form, which separates as a silky crystalline solid resembling asbestos. The unstable variety can only be made by vaporising the β-form. The β-form boils at a considerably higher temperature than α-SO_3. Both varieties fume strongly in air, owing to their volatile and hygroscopic nature. According to the work of Le Blanc and Rühle,[1] and of Smits,[2] there are three forms of sulphur trioxide melting at 62.2,° 32.5° and 16.8° respectively. They differ also in their vapour pressures and may be isolated from the gaseous state under different conditions. The persistence of these forms in the presence of each other and of the liquid is remarkable, so that, for instance, at 25° the most varied vapour pressures may be given by an apparently permanent form of SO_3. The properties of a sample of solid SO_3 depend on its previous history, and at temperatures below 0° the most arbitrary vapour pressures, ranging from 20 to 195 mm., may be found; it has not without reason been described as a chemical chameleon. The conversion of one form into the other does, however, occur, and sometimes the form which melts at 16.8° gives sudden, almost explosive, variations in the vapour pressure, which are explained by the production of forms of high and of low vapour pressure at the same time. The form of high melting point is well known to be less active, so much so that the sharp outline of the needles is preserved for some hours even in moist air. It has been suggested that the form of low melting point has a trimeric structure while the β-form melting at 32.50 has a chain structure. The polymers are dissociated in the gaseous state.

Sulphur trioxide is a powerful oxidising agent, and sets fire to phosphorus. The trioxide forms SO_2 and O_2 when strongly heated, but, in the absence of a catalyst, a very high temperature is required for complete decomposition. Free sulphur is absorbed by SO_3 with the formation of a brown colloidal liquid, but this is formed only in the presence of small quantities of water. Under other conditions the sulphur combines with the trioxide to form the bluish-green *sulphur sesquioxide* $(S_2O_3)_x$, a very reactive and unstable substance which with water gives free sulphur and mixtures of sulphur acids.[3]   Vogel and

[1] *Ber. Sächs. Akad. Wiss.*, 1922, 75, 106.
[2] *J. Chem. Soc.*, 1926, 128, 1180, 1603.
[3] Vogel and Partington, *J. Chem. Soc.*, 1925, 127, 1514.

Partington failed to obtain SO from S_2O_3, but Wöhler and Wegwitz[1] found that from 40°-80° the simultaneous reactions proceed:

$$S_2O_3 \longrightarrow SO + SO_2 \text{ (4 parts)}$$
$$S_2O_3 \longrightarrow S + SO_3 \text{ (1 part)}.$$
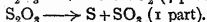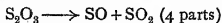
Iodine, selenium and tellurium are also absorbed by sulphur trioxide with the production of colloidal solutions. The compounds of SO_3 with H_2SO_4 are described on pp. 586-587.

Selenium trioxide, SeO_3,—After many fruitless attempts to prepare this oxide it was made by Rheinboldt, Hessel and Schwenzer.[2] It is formed together with the dioxide by treating grey selenium with oxygen under the influence of a high frequency discharge. The trioxide is white and extremely hygroscopic.

Tellurium trioxide, TeO_3, is formed by heating telluric acid to a moderate temperature. It is an orange solid similar in appearance to telluric acid; heated to a higher temperature, a residue of TeO_2 is obtained. TeO_3 is insoluble in water, and in dilute alkalis and acids. It dissolves in strong alkalis with the formation of tellurates.

Sulphuric Acid, H_2SO_4.—*Preparation.*

—This acid is formed by the action of water on sulphur trioxide: $SO_3 + H_2O \longrightarrow H_2SO_4$, and also by the oxidation of sulphur, hydrogen sulphide, lower acids of sulphur (*e.g.* $H_2S_2O_4$, $H_2S_2O_3$, $H_2S_2O_3$) and of polythionic acids in the presence of water. Sulphurous acid is slowly oxidised by the air to sulphuric acid, but usually stronger oxidising agents are required—halogens, hypochlorites, nitric acid, chloric acid, permanganic or chromic acids. The manufacture of sulphuric acid by the *contact process* has been described (see p. 566). The only other method used on the large scale is the *lead chamber process*. This depends upon the oxidation of sulphur dioxide by nitric acid in the presence of water.

The sulphur dioxide used in the lead chamber process is obtained by the combustion of sulphur, of "spent oxide," or of pyrites (FeS_2). Iron pyrites contains a large percentage of sulphur, and burns spontaneously when once ignited, provided there is a sufficient draught of air. Almost the whole of the sulphur is oxidised and Fe_2O_3 is left as a residue. Copper pyrites, $CuFeS_2$, may be substituted for FeS_2, and other sulphide ores can also be used—*e.g.* lead glance, PbS, and zinc blende, ZnS—but these are less efficient, as the first products of roasting are the sulphates which are decomposed only at a very high temperature.

The SO_2, mixed with air, is first conveyed to the Glover tower and then into a system of two or three chambers made of sheet lead, which are connected in series and have a total capacity of several thousand cubic metres. Steam or water in a fine spray is blown into the lead chambers, and it is here that the sulphur dioxide is oxidised by nitric acid to sulphuric acid, the oxidising agent being reduced to lower oxides of nitrogen, which are subsequently reoxidised by air to higher oxides. If ideal conditions could be realised the nitric acid would be reduced

[1] *Z. anorg. Chem.*, 1933, 213, 129.
[2] *Ber.*, 1930, 63, 1865.

solely to NO, but in practice part of the acid suffers further reduction, and traces of ammonia and nitrogen are sometimes formed. Reduction products which contain less oxygen than nitric oxide, such as N_2O and free nitrogen, are not oxidised by the air. The so-called chamber crystals, possibly nitrosylsulphuric acid (p. 645), are formed if the supply of water is deficient. The compound is decomposed by more steam into sulphuric acid and nitrogen trioxide:

$$N_2O_3 + 2SO_2 + O_2 + H_2O \longrightarrow 2HO . SO_3 . ONO,$$
$$HO . SO_2 . ONO + H_2O \longrightarrow HO . SO_2 . OH + HNO_2,$$
$$2HNO_2 \longrightarrow H_2O + NO_2 + NO.$$
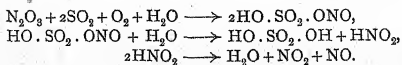
The exit gases from the lead chambers contain a large proportion of nitric oxide, and are passed up a tower packed with pieces of coke or earthenware balls, down which 75-80 per cent. sulphuric acid is allowed to trickle. This section of the plant is known as the Gay-Lussac tower. The acid absorbs the nitrous fumes as they ascend the tower, and the "nitrous vitriol" that collects at the bottom is pumped to the top of the Glover tower, situated between the pyrites burners and the first lead chamber. The functions of this tower are: (1) The oxidation of the nitric oxide to the higher oxides of nitrogen by the excess of air in the gases from the burners; (2) the cooling of the hot gases down to about 50°, the requisite temperature for the lead chamber reaction; (3) the concentration of the sulphuric acid.

The chemistry of the chamber process of manufacture may thus be approximately represented as a recurring cycle of operations. The sulphur dioxide is first oxidised by nitric acid; the reduction products of the nitric acid are reoxidised by air to the higher oxides of nitrogen. The original theory of the catalytic influence of the nitrogen compounds assumed that NO_2 was formed as an intermediate product [1]:

I. $HNO_3 \longrightarrow NO.$ II. $NO + O \longrightarrow NO_2.$
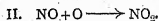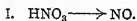
This simple hypothesis is unsatisfactory, because no explanation is given of the formation of the lead chamber crystals and their subsequent decomposition into sulphuric acid. It was for a long time believed that the intermediate product consisted of nitrosylsulphuric acid; actually the reactions which occur in the lead chambers are still more complicated. Many explanations have been devised; the most important are those due to Raschig,[2] and Lunge and Berl.[3] Mention may also be made of Neumann's work.[4]

Raschig states that the chamber crystals do not possess the formula $HO . SO_2 . O . NO$, but have a structure in which the nitrogen is directly linked to sulphur, viz. $HO . SO_2 . NO_2$ (cf. pp. 644-646). Chemically, this compound is nitrosulphonic acid. The compounds formed by reduction are assumed to be:

$$O . ON . SO_2OH \qquad\qquad ON . SO_2OH$$
Hydroxy-nitrosulphonic acid.   Nitrososulphonic acid.
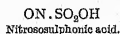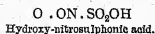
According to Raschig, nitrous acid is produced in the Glover tower by the hydrolysis

[1] Péligot, Ann. Chim. Phys. (3), 1844, 12, 263.
[2] Z. angew. Chem., 1904, 17, 1398; 1905, 18, 1281.
[3] Ibid., 1906, 19, 807.
[4] Ibid., 1906, 19, 1702.

of nitrosulphonic acid $HO . SO_2 . NO_2 + H_2O \longrightarrow HO . SO_2 . OH + ON . OH$; then the following cycle of chemical reactions takes place :

I. Nitrous acid unites with SO_2 to form nitrosulphonic acid

$$ON . OH + SO_2 \longrightarrow ON . SO_2 . OH.$$

II. The nitroso-acid then reacts with a further quantity of nitrous acid, giving hydroxy-nitrosulphonic acid

$$ON . SO_2 . OH + ON . OH \longrightarrow (HO)ON . SO_2 . OH + NO.$$
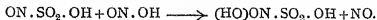
III. This compound decomposes with production of sulphuric acid

$$(HO) . ON . SO_2 . OH \longrightarrow NO + H_2SO_4.$$
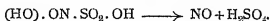
IV. Finally, the nitric oxide is oxidised to nitrous acid by the air,

$$2NO + O + H_2O \longrightarrow 2ON . OH.$$
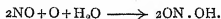
The original paper must be consulted for the arguments upon which Raschig bases his theory ; his supposition, however, that nitrous acid is formed as an intermediate product is open to considerable objection, for it is probably unstable at the temperature of the lead chambers, and even the existence of nitrosulphonic acid is doubtful ; and if the old formula for the lead chamber crystals is incorrect (p. 645) there is even less foundation for Raschig's theory.

Lunge and Berl assume that hydroxynitro-sulphonic acid, which is a definite compound, is produced by the interaction of sulphur dioxide with nitrous fumes :

I. $SO_2 + NO_2 + H_2O \longrightarrow HO . SO_2 . NO(OH).$

By further oxidation nitrosulphonic acid is obtained ; this is then converted into nitrosylsulphuric acid by isomeric change :

II. $2HO . SO_2 . NO(OH) + O \longrightarrow H_2O + 2HO . SO_2 . NO_2 \longrightarrow 2HO . SO_2 . ONO.$
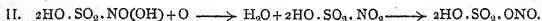
The necessary oxygen for this reaction may be supplied either by the air or by NO_2. The next step consists in the formation of sulphuric acid. When excess of steam is present the reaction, already discussed, is represented by the equation :

IIIa. $HO . SO_2 . ONO + H_2O \longrightarrow HO . SO_2 . OH + HNO_2.$
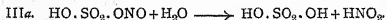
Hydroxy-nitrosulphonic acid is formed in addition, if SO_2 is in excess :

IIIb. $2HO . SO_2 . ONO + SO_2 + 2H_2O \longrightarrow HO . SO_2 . OH + 2HO . SO_2 . NO(OH).$

The cycle then begins over again. Any nitric oxide produced by reduction of NO_2 is reoxidised by air. The general course of the reaction is clearly determined by the relative quantities of the reacting gases in the different portions of the plant. Those zones in which an oxidising effect occurs contain a large proportion of higher nitrogen oxides, while the reducing zones are charged with excess of sulphur dioxide and there is some evidence that the main reactions occur in the liquid and not in the gaseous parts of the system.

Sulphuric acid manufactured by the chamber process contains various impurities, among which are oxides of nitrogen derived from the nitric acid. These are eliminated by treatment with a little ammonium sulphate : ; $2NH_3 + N_2O_3 \longrightarrow 2N_2 + 3H_2O$; the nitrogen is expelled by warming the acid. Other impurities, which are derived from the pyrites, include arsenic, antimony, copper and lead, and are more difficult to remove. Much of the lead which is present results from the solvent action of the acid upon the lead used in the construction of the plant. These metals can be precipitated by hydrogen sulphide or thiosulphate after previous dilution of the acid. The arsenic is found partly in the tervalent and partly in the quinquevalent

state. The zones where sulphur dioxide predominate give tervalent arsenic, while the quinquevalent derivatives are formed during the passage of the acid through oxidising regions. Tervalent arsenic is eliminated in the form of the volatile trichloride, $AsCl_3$, which is produced either by adding common salt or, if it is undesirable that the acid should contain sodium, by passing a current of HCl gas through the hot liquid. Quinquevalent arsenic, as well as the heavy metals, could be separated as a non-volatile residue by distillation, but this process is too costly to be used on the large scale. When the percentage of lead is high the greater part is precipitated as $PbSO_4$ by diluting the chamber acid.

The chamber acid contains about 65 per cent. H_2SO_4 (55°-60° Bé). This acid can be concentrated further either in the Glover tower or by heating it in leaden pans till it contains about 80 per cent. of H_2SO_4. A stronger acid than this attacks the lead rather rapidly; the acid is then heated in quartz basins. Modern methods consist in running the acid down towers or steps made of volvic stone, and at the same time forcing hot gases from a coke furnace in the opposite direction. The final concentration can be effected in gilded platinum vessels; by this means 98 per cent. sulphuric acid is obtained. (Density 1·84.) Concentrated sulphuric acid attacks gold less rapidly than platinum. Iron containers can be substituted for those of platinum in the concentration of fairly concentrated acid, especially fuming sulphuric acid; the iron assumes a passive condition even in contact with the non-fuming concentrated acid. Cast iron vessels must not be used for the storage of the fuming acid, as the acid gets into the pores of the iron, and hydrogen, hydrogen sulphide and sulphur dioxide are slowly formed by chemical action until, finally, the internal pressure is sufficiently great to shatter the receptacle with a loud explosion. Wrought iron is more readily attacked than cast iron by the fuming acid, unless more than 27 per cent. of free SO_3 is present; then the iron becomes passive again. The passivity is shown by conductivity measurements to be connected with the degree of dissociation of the acid. Pure H_2SO_4 is scarcely ionised at all; up to a certain point ionisation can be increased by addition of either H_2O or SO_3 and is accompanied by greater chemical activity; consequently, sulphuric acid which is dissociated to a considerable extent attacks iron, but the non-ionised acid renders the metal inert. It is found that the conductivity of H_2SO_4 again decreases when the quantity of free SO_3 exceeds a certain limit (cf. Fig. 57, p. 573).

Pure sulphuric acid can be obtained by cooling the acid until crystals of 100 per cent. H_2SO_4 separate.

Properties.—Concentrated sulphuric acid is a colourless, odourless, somewhat viscous liquid, which does not fume in the air. The variation of important physical properties with concentration is illustrated in the diagram on page 573. It may be observed that formation of oleum or fuming acid by dissolving SO_3 in 100 per cent. H_2SO_4 does not break the continuity of many of the curves.

Maxima on the freezing point curve (1) occur with liquids of the compositions:

	$H_2SO_4 . 4H_2O$	$H_2SO_4 . H_2O$	H_2SO_4	$H_2SO_4 . SO_3$
Melting point .	$< 0°$	$+ 8°$	$+ 10°$	$+ 36°$

The eutectic mixture between H_2SO_4 and $H_2SO_4 . H_2O$ melts at $-22°$, and corresponds closely to the formula $2H_2SO_4 . H_2O$, the ordinary acid of commerce (66° Bé); the eutectic temperature between $H_2SO_4 . H_2O$ and $H_2SO_4 . 4H_2O$ is below $-50°$; hence dilute sulphuric acid and
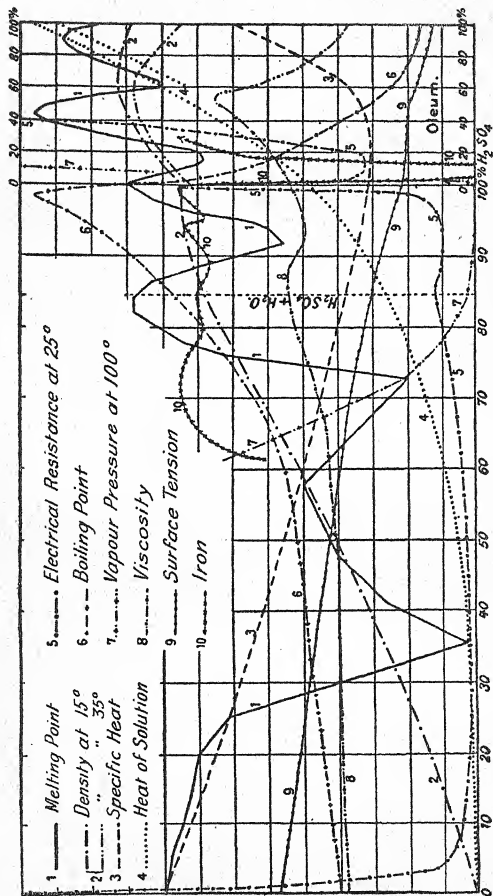
FIG. 57.—Physical properties of sulphuric acid of various concentrations.

1 — Melting Point
2 — Density at 15°
" " 35°
3 — Specific Heat
4 — Heat of Solution
5 — Electrical Resistance at 25°
6 — Boiling Point
7 — Vapour Pressure at 100°
8 — Viscosity
9 — Surface Tension
10 — Iron

snow make good freezing mixtures. Finally, the eutectic mixture between H_2SO_4 and $H_2S_2O_7$ melts at $-12°$. All these compounds and mixtures are easily undercooled in the liquid condition; e.g. the eutectic mixture between H_2SO_4 and the monohydrate may be undercooled to $-47°$, that between H_2SO_4 and $H_2S_2O_7$ to $-26°$. It is thus difficult to obtain pure H_2SO_4 in the solid state, although the true freezing point is not far below room temperature. The crystals which separate before the eutectic mixtures are true hydrates of sulphuric acid.

The boiling point curve (6) is interesting, and has a pronounced maximum at a point where the acid contains 98·3 per cent. H_2SO_4; this concentration is obtained whether a stronger or a weaker acid is distilled. With stronger acid, SO_3 distils off first, and with weaker acid, water, thus showing the same relations as for hydrochloric acid (p. 223), and nitric acid (p. 687). If 100 per cent. acid is prepared by passing SO_3 into ordinary "concentrated" sulphuric acid, the product is unstable and tends to give off SO_3. At a pressure approaching 755 mm. the boiling points of sulphuric acid are as follows:

% H_2SO_4	.	.	61·7	81·5	96·2	98·5	99·9	...	...	...
Pure H_2SO_4 + % SO_3	.	...	...	...	...	...	3·6	26·2	63·2
Boiling point	.	.	140°	202°	292°	317°	273°	212°	125°	60°

The vapour pressure of 98·3 per cent. sulphuric acid is also exceptionally small at lower temperatures, and the acid does not evaporate in air to any marked extent, but takes up water till its vapour pressure becomes equal to that of the water in the atmosphere above it. As the vapour pressures of acids of various concentrations are known, that of other substances containing water, e.g. salts with water of crystallisation, can be estimated by keeping them over sulphuric acid of varying concentrations in closed vessels; if the sulphuric acid neither increases nor decreases in weight the vapour pressure of the salt is the same as that of the sulphuric acid used. The vapour pressure of sulphuric acid above 88 per cent. strength is less than 1 mm. mercury at room temperature, while that of 60 per cent. acid only amounts to 3 mm. Concentrated sulphuric acid is therefore a most efficient dehydrating agent; it not only takes up moisture from the air, but also removes the elements of water when they are present in chemical compounds. For example, carbohydrates are carbonised (paper, wood, sugar). When sulphuric acid is poured into water much heat is evolved as the hydrates already mentioned are formed. The heat of solution of 1 mole of sulphuric acid in varying quantities of water is as follows:

Moles H_2O	.	.	1	2	3	5	9	19	∞
Cal.	.	.	6·27	9·36	11·11	13·1	14·9	16·2	18·0

As compounds are formed there is an appreciable contraction when the acid is mixed with water. This shows a maximum value at about

the concentration $H_2SO_4 . 2H_2O$, but is not conclusive evidence that this hydrate exists, as the marked dissociation which takes place at this dilution can have a preponderating effect both on the volume change and on the evolution of heat.

The density of sulphuric acid at the following concentrations is:

Conc. 9·8   19·6   29·8   39·8   50·1   60·2   70·3   80·2   90·09   98·2 per cent.
d.   1·067 1·14   1·22   1·30   1·40   1·50   1·62   1·73   1·82   1·84   ,,

Other physical properties may be seen from the diagram on p. 573.

Structure of the SO_4^- Ion, and other Oxyacid Ions of Sulphur.

The simple electronic structure $\left[\ddot{\underset{..}{O}} \, \underset{..}{\overset{..}{S}} \, \ddot{\underset{..}{O}} \right]$, built in accordance with the octet rule, is insufficient to account for the observed interatomic distances in the sulphate ion. These distances are smaller than is compatible with a single covalent bond, and indicate some double-bonded character in the S—O bond. While, in addition to the above structures, others like
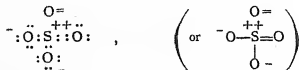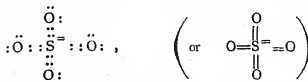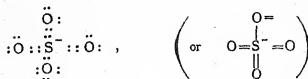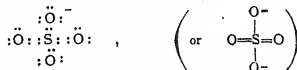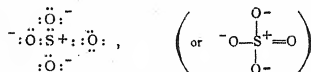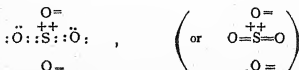
also contribute to the normal state of the ion; the whole may be regarded simply as a resonance hybrid involving some single and some double bonds, the latter resonating between the four available positions. This makes a reasonable explanation of

the shortening of the interatomic distance, and a similar treatment of the SO_2 molecule also leads to a resonance hybrid:

$$\left\{ S \underset{O}{\overset{O}{<}} \ , \ S \underset{O}{\overset{O}{<}} \right\} .$$
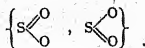
The $S_3O_6^=$ ion is to be regarded as

$$-: \overset{\overset{\ddot{O}:}{\parallel}}{\underset{\underset{\ddot{O}:}{\parallel}}{\ddot{O}}} - \overset{..}{S} - \overset{\overset{\ddot{O}:}{\parallel}}{\underset{\underset{\ddot{O}:}{\parallel}}{\ddot{S}}} - \overset{..}{S} - \ddot{O}: -,$$
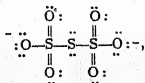
in which, again the double bonds resonate between the six available positions, making all the S—O bonds equivalent.

$S_2O_5^=$ and $S_2O_6^=$ are to be written:

$$\left[O - \overset{\overset{O}{\parallel}}{\underset{\underset{O}{}}{\overset{..}{S}}} - \overset{\overset{O}{\parallel}}{S} - O \right]^= \quad \text{and} \quad \left[O - \overset{\overset{O}{}}{\underset{\underset{O}{}}{S}} - \overset{\overset{O}{}}{\underset{\underset{O}{}}{S}} - O \right]^-$$
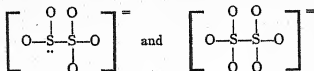
respectively.

The chemical behaviour of sulphuric acid is conditioned by its power for withdrawing water, by its acid character and by the possibility of reducing it. It is a strong dibasic acid, but hydrogen halides, chloric acid, perchloric acid and a few others exceed it in the extent of their ionic dissociation. At a moderate dilution one hydrogen atom dissociates first; on further dilution, more and more SO_4'' ions appear (for its conductivity, cf. Fig. 57). If, as a result of dilution, sufficient quantities of H ions are present, hydrogen is liberated from the acid by those metals which are above hydrogen in the electro-chemical series (cf. p. 151); otherwise it is reduced to SO_2, usually only on warming (p. 546). The effect of sulphuric acid on iron is mentioned on p. 154. No metal is absolutely resistant to hot concentrated sulphuric acid, but gold is attacked least. Very often the action is exceptionally slow, and many base metals, like iron, become almost completely passive in the acid, or become covered with a thin, insoluble film of sulphate, at least at certain concentrations of the acid. This takes place with lead, but the lead sulphate is soluble in stronger acid with the formation of an acid sulphate. Other metals, like zinc and copper, do not become passive in the acid. On heating, sulphur dioxide is evolved, and a similar action occurs with many non-metals, especially phosphorus, amorphous carbon and sulphur. Selenium and tellurium dissolve in the acid to give coloured colloidal solutions, but these elements are also oxidised later. Definite reducing agents, such as hydrogen iodide, reduce concentrated sulphuric acid beyond the SO_2 stage, giving H_2S, which then yields free sulphur with the SO_2 present.

The hydroxyl groups of sulphuric acid may be replaced by chlorine, fluorine, NH_2 or other radicals containing nitrogen; these are discussed on pp. 594, 641.

OXYGEN COMPOUNDS OF S, Se, Te (*continued*):
HALOGEN COMPOUNDS

Sulphates—Pyrosulphuric acid—Selenic acid—Telluric acid—Perdisulphuric acid and Caro's acid—Halogen derivatives of the sulphur acids—Halides of sulphur, selenium and tellurium

Sulphates

UNLIKE thiosulphuric acid, the polythionic acids and hyposulphurous acid, sulphuric acid forms acid salts of the type $MHSO_4$ as well as the normal sulphates M_2SO_4. In the sulphates of the alkali metals, indeed, there is yet a further series of "super-acid" salts such as $MH_3(SO_4)_2$, $M_4H_2(SO_4)_3$, etc. These compounds can be compared with the acid fluorides, chlorides and nitrates. Many sulphates which have the empirical formula of the normal salt are really derived from complex metal-sulphuric acids. Basic sulphates of the less electropositive metals are also known.

Preparation.—Sulphates are obtained by the action of sulphuric acid on the oxides or hydroxides, and also by double decomposition between sulphuric acid and salts of more volatile acids. Carbonic acid may thus be driven out even from dilute solutions. Dry chlorides also give sulphates with sulphuric acid; if the acid formed is miscible with sulphuric acid (*e.g.* HNO_3), it escapes only on heating. Sulphates are further produced by the oxidation of all other sulphur compounds of the metals, in solution as well as on heating in air. A solution of ammonium sulphide may be completely converted to sulphate by pumping in air under 10 atm. pressure at 100°.

Some technically important sulphates, especially potassium sulphate, K_2SO_4 and Epsom salt, $MgSO_4$, $7H_2O$, are obtained directly from the natural products in the Stassfurt beds (p. 259). Potassium sulphate is obtained, in principle, in the following way: the "Abraumsalze" containing potassium chloride are decomposed with sulphates ($MgSO_4$ or $CaSO_4$), when K_2SO_4 crystallises out, as it is only moderately soluble. Schönite, $K_2Mg(SO_4)_2$, $6H_2O$, is frequently used for this preparation; with potassium chloride it gives a solution of magnesium chloride and a precipitate of potassium sulphate. Sodium sulphate, Glauber's salt, Na_2SO_4, $10H_2O$, is similarly obtained by double decomposition between NaCl and $MgSO_4$. Glauber's salt is easily soluble at moderate tem-

peratures, so the mixed solution is cooled to $-3°$, when it is deposited, while $MgCl_2$ remains in solution. Sometimes NaCl is directly decomposed with H_2SO_4, and it is further possible to obtain sodium sulphate by passing sulphur dioxide mixed with air and steam over solid NaCl (Hargreave's Process); it is then unnecessary to start with finished sulphuric acid. The more insoluble sulphates appear as such in nature; *e.g.* the barium salt (barytes, heavy spar), strontium sulphate (celestine), calcium sulphate (gypsum, anhydrite, selenite) and lead sulphate (anglesite). Besides these, silver sulphate has a fairly low solubility, but all other sulphates are moderately soluble, though much less so than the corresponding chlorides (with the exception of Na_2SO_4), and only a few are hygroscopic. The sulphates of bismuth, antimony and mercury deposit basic salts by the action of water, so that they are obtainable only from acid solution.

Water Content and Solubility.—The sulphates of Bi, Sb, Hg, as well as the sparingly soluble Ba, Sr, Pb and Ag salts, are anhydrous, while calcium sulphate can take up 2 mols. of water. Further, thallous sulphate and the alkali sulphates are anhydrous, with the exception of sodium sulphate. Li_2SO_4 can take up 1 mol. H_2O. The other soluble sulphates all contain water; those of the bivalent metals, Mg, Mn, Fe, Ni, Co, Zn, V, usually crystallise with 7 mols. water, and in this form are described as vitriols. Nearly all these, however, form crystals with 6 mols. H_2O, and the stability limits of the hexa- and hepta-hydrates lie very close together. Other hydrates with still less water frequently appear at higher temperatures; thus, magnesium sulphate gives compounds with 1 mol. H_2O (kieserite), with 5/4, 2, 4, 5 mols. H_2O, two different forms with $6H_2O$, two with $7H_2O$, and finally a hydrate with $12H_2O$, as well as the anhydrous salt. Manganese sulphate, similarly, gives salts with 0, 1, 2, 3, 4, 5 and 7 mols. H_2O. It is noteworthy that copper sulphate contains only 5 mols. H_2O and cannot take up more water. Many vitriols retain the last molecule of water very firmly on heating. This water was previously called water of constitution. Among the sulphates of bivalent metals the composition of normal cadmium sulphate, $3CdSO_4$, $8H_2O$ is of special interest. There are many other hydrates of cadmium sulphate, including one with 7 mols. H_2O. The sulphates of tervalent metals are richest in water; thus, besides anhydrous $Al_2(SO_4)_3$, hydrates with 6, 10, 16, 18 and 27 mols. H_2O have been described; here the 18-hydrate is the one which crystallises at normal temperatures.

In the sulphates which form several hydrates the solubility of the individual hydrates has often been determined, but only the more important results will be dealt with here. It is often found that the solubility of anhydrous sulphates decreases with rise in temperature.

Sodium sulphate is characteristic. The transition point between the anhydrous salt and the 10-hydrate lies very sharply defined at $32.384°$, that of Na_2SO_4. $10D_2O$ is

at 34·48°. Above this temperature Na_2SO_4 always crystallises free from water. In 100 g. H_2O at 35°, the solution contains 49·4, and at 100° only 42·7 g. Na_2SO_4. On the other hand, the solubility of Glauber's salt, $Na_2SO_4 . 10H_2O$, increases very rapidly with rising temperature, since 100 g. water at 0° take up 5, and at 30°, 40 g. of the salt. The solubility curve thus shows a very marked maximum at the transition point. If a solution of the anhydrous salt is gradually cooled below the transition point, it crystallises if nuclei of Glauber's salt are present, but if these are excluded the solution becomes more and more supersaturated, since the solubility rises with falling temperature. This undercooling may be very easily carried out if a closed vessel containing Glauber's salt and water is first heated above the transition point, to remove any Glauber's salt nuclei. The solution can then remain at room temperature for years in the undercooled condition, and only crystallises accidentally. If, however, the vessel is opened so that atmospheric dust may float in, the supersaturation is very soon removed, as there are Glauber's salt nuclei in the dust. Besides the forms of Na_2SO_4 mentioned, there is a further hydrate with 7 mols. H_2O. This is always labile; its solubility curve, like that of the 10-hydrate, rises with temperature, but at all points lies above that of Glauber's salt; since the less soluble form is always more stable, Na_2SO_4, $7H_2O$ can pass into Na_2SO_4, $10H_2O$ at all temperatures. It is only formed as an intermediate stage, but it can always be kept so that its special solubility curve can be confirmed— an indication that the different hydrates occur as such in solution. Of the 7-hydrate, 100 g. water at 0° dissolves 19·6 g., and at 20°, 44·7 g.; the point of intersection of the solubility curves of the 7-hydrate and the anhydrous salt lies at 24·4°; above this temperature, the 7-hydrate can be directly converted into the anhydrous salt, while below this temperature it passes into the 10-hydrate.

Such complications do not appear in the other alkali sulphates, as they occur only as anhydrous salts. Potassium sulphate has a very sparing solubility; the solubility increases with increasing atomic weight up to caesium sulphate. A few characteristic values are given below. 100 g. water dissolves :—

Temp.	K_2SO_4	Rb_2SO_4	$(NH_4)_2SO_4$	Cs_2SO_4
0°	7·35	36·4	71·0	167 g.
100°	24·1	81·8	97·5	220 „

The solubility of anhydrous lithium sulphate is comparable with that of sodium sulphate, as it also diminishes with rising temperature; 100 g. water dissolve at 0°, 35·3 g., at 100° only 29·4 g. of the salt. The falling-off in solubility with increasing temperature takes place less rapidly than the rise in solubility, which is so much more common. A very good example of the falling-off in solubility of sulphates, even when they are hydrated, is given by the rare earths (cf. p. 432).

The solubility relations in gypsum, $CaSO_4, 2H_2O$, are very remarkable. Here the solubility increases up to about 38°, and decreases again without any change in the water content of the solid above this temperature. There are obviously several superimposed factors conditioning the path of the solubility curve. 100 g. water dissolve :—

Temp.	0°	18°	40°	55°	75°	100°
$CaSO_4$	0·176	0·202	0·210	0·201	0·185	0·162 g.

Calcium sulphate has several other hydrates, but these do not appear during a normal investigation of solubility owing to the marked delay in transformation; the transition points also lie far removed from 38°. There is a hydrate of the formula $2CaSO_4 . 1H_2O$ (hemi-hydrate, plaster of Paris), which is formed from the dihydrate at 107°, and also two forms of anhydrous gypsum,[1] of which one is formed from the

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[1] See Caspari, *Nature*, 1934, 133, 648.

dihydrate at 66° and the other at 89°. The passage of the dihydrate into hemi-hydrate takes place only after long delay, and does not even begin below 130°.[1] This hemi-hydrate is the chief constituent of burnt gypsum. If a higher dehydrating temperature is applied the time for hardening increases, and after heating to red heat the plaster is dead burnt; the relationships here are similar to those in the burning of lime (p. 799). By burning anhydrite at 1000°-1300°, however, a solid solution of CaO in anhydrite is formed, which hardens slowly (Keene's cement, flooring plaster).

When precipitated simultaneously with barium sulphate a greater quantity of calcium sulphate comes down than when it is precipitated alone. Further, when barium sulphate is precipitated in presence of calcium it always contains that element, and solutions which ordinarily dissolve calcium sulphate fail to remove it from this precipitate.

The solubility of the sparingly soluble sulphates of barium, strontium and lead increases with rising temperature. It is so small that it can be estimated only by conductivity measurements. At 18°, 100 g. solution contain :

$$BaSO_4 \quad . \quad 0.23 \text{ mg.} \qquad PbSO_4 \quad . \quad 4.6 \text{ mg.} \qquad SrSO_4 \quad . \quad 11.4 \text{ mg.}$$

These solubilities are still further diminished by the addition of alcohol. A saturated solution of silver sulphate contains 0.727 g. of the salt per 100 c.c. at 18°.

For some ammines of sulphates see p. 271.

Many of the acid sulphates are much more easily soluble in water. Those of the alkalis are readily soluble, and about 5 g. $BaSO_4$ dissolves in 100 g. cold conc. sulphuric acid, and on warming considerably more. From this solution the salt $Ba(HSO_4)_2$ is obtained, like the analogous strontium and calcium compounds, in well-crystallised forms. If, however, water is added to them, they immediately decompose into the normal salt and free sulphuric acid. The alkali bisulphates are also decomposed by water, and by repeated recrystallisation the normal salt may be obtained from them. The stability of the complex is thus only slight, like that of the alums and other "double salts" of sulphuric acid. A notable exception is the very stable hydrazine sulphate $N_2H_4 . H_2SO_4$, which might, however, be $\left(\begin{array}{c} NH_3 \\ | \\ NH_3 \end{array}\right) SO_4$ and not $(NH_2 . NH_3) HSO_4$; only 3.0 parts of this compound dissolve in 100 parts water at 22°. Normal hydrazine sulphate, $2N_2H_4 . H_2SO_4$, in contrast to this, is very deliquescent; the relations here are thus the reverse of those which usually obtain.

Other Properties.—Some sulphates form large, clear, well-defined crystals, *e.g.* Glauber's salt, copper and iron vitriols. In others the crystals only attain a medium size even with careful cultivation, *e.g.* ammonium sulphate and potassium sulphate, which is isomorphous with it, giving clear crystals which are difficult to powder and show triboluminescence. The sparingly soluble sulphates, especially barium and strontium sulphates, yield quite small crystals. The sulphates are isomorphous with the selenates, chromates and manganates, but not with the tellurates. Barium sulphate can be obtained in colloidal

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[1] Van 't Hoff and collaborators, *Z. physikal. Chem.*, 1903, 45, 257.

form, as a gel, by precipitating a methyl alcohol solution of barium hydroxide with sulphuric acid.

The soluble sulphates have a saline taste, as long as it is not overcome by the acid taste of sulphuric acid, due to hydrolysis (*e.g.* $(NH_4)_2SO_4$, Li_2SO_4), often with a bitter tang (Na_2SO_4, K_2SO_4, $MgSO_4$). On heating, the sulphates of the base metals give off SO_3 more or less easily; $CaSO_4$ is converted at white heat to CaO, but $BaSO_4$ only above $1500°$. The alkali sulphates are volatile without decomposition at high temperatures, and fuse at lower temperatures:

	Li_2SO_4	Na_2SO_4	K_2SO_4
Melting point	$859°$	$897°$	$1074°$;

the acid sulphates have very much lower melting points, perhaps because they decompose. Thus the compound $2LiHSO_4 . H_2SO_4$ melts at $110°$, $KHSO_4$ at about $200°$, so that molten acid sulphates of the alkali metals may be used for high temperature baths. Those which contain much sulphuric acid fume strongly at higher temperatures, and may lose water passing to pyrosulphates. The ammonium salt shows no definite melting point, since it gives off ammonia before melting. Hydrazine sulphate, in melting as in solubility, does not conform to rule, and the acid salt melts at a higher temperature ($254°$) than the normal ($85°$). Many heavy metal sulphates are quite stable at a moderate heat, and can therefore be used in quantitative analysis. Thus the sulphates of magnesium, manganese, cadmium, lead, cobalt (and less easily those of nickel, copper or zinc), may be converted by heat into anhydrous forms still containing all their SO_3. It is more difficult, but not impossible, to dehydrate aluminium, chromium and tervalent iron sulphates without loss of sulphuric acid.

Hydrogen or carbon reduces many anhydrous sulphates to sulphide on heating, provided they are not directly converted to the metal.

Complex Sulphates.—The acid sulphates are often complex compounds. Even normal sulphates, at least those of metals of higher valency, often have a complex structure, as may be seen from the formula of hydrated cadmium sulphate: $3CdSO_4 . 8H_2O$, or from that of a magnesium sulphate, $4MgSO_4 . 5H_2O$. In acid salts of the form $MHSO_4$, their complex character cannot be recognised from their formulae. Such salts are often found, especially among the alkalis and the alkaline earths. Besides these acid salts, however, a whole series with more complicated composition is known; thus, the potassium compounds

$$3K_2SO_4 . H_2SO_4 \qquad 2K_2SO_4 . H_2SO_4 \qquad 5K_2SO_4 . 3H_2SO_4$$
$$4K_2SO_4 . 3H_2SO_4 \qquad K_2SO_4 . 3H_2SO_4$$
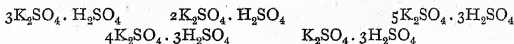
the sodium salts $Na_2SO_4 . 2H_2SO_4$ and $Na_2SO_4 . 3H_2SO_4$ have been

described,[1] and calcium forms the bisulphate $CaSO_4 . H_2SO_4$, and the more acid salt $CaSO_4 . 3H_2SO_4$. These compounds are to be regarded as metal-sulphuric acids (sulphato-acids). The hydrogen they contain can be replaced by a metal different from that already present, and in this way a large class of double sulphates is formed. The most important are those which contain alkali and alkaline earth metals, and one series of the Stassfurt "Abraumsalze" belong to this class (p. 259). They are not very stable as complexes and readily break up into their constituents when dissolved in water. Double salts of the schönite type and the alums are only slightly complex in aqueous solution. Normal $BeSO_4$, $4H_2O$, i.e. [Be, $4H_2O$] SO_4 dissolves beryllia forming the complex sulphate,[2] [Be, 4BeO] SO_4.

The study of the internal structure of these complex salts is difficult, but it is rather simpler in the compounds of the tervalent metals, of which those of chromium will be considered in detail. Compounds which contain the sulphate of empirical formula $Cr_2(SO_4)_3$, aq. exist in green and violet forms like the corresponding chlorides (p. 292). The violet chromium sulphate crystallises readily in octahedra, is easily soluble in water and has the composition $Cr_2(SO_4)_3 . 18H_2O$. The green form, on the other hand, does not crystallise, but forms gummy or gelatinous films on evaporating the solution. The violet form is obtained when $Cr(OH)_3$ is dissolved in concentrated sulphuric acid, and the crystals which separate are taken up in water and precipitated by alcohol. The green form is obtained when the violet form is dehydrated at a moderate temperature. It becomes thereby less soluble in water, and if the drying is carried out at 140° the product is quite insoluble in ice water. Solutions of the violet form are a bluish violet, while those of the green form are invariably a pure green. At 20° one part of the violet salt dissolves in 0·83 parts of water, and barium chloride precipitates the whole of the SO_4, while only a part is precipitated from solutions of the green salt; the actual quantity depends on the temperature to which it has previously been heated. This leads to the conclusion that in the green salt some of the SO_4 has passed into the cation to form a complex, while in the violet form the whole of the SO_4 is present as anions; this conclusion is supported by conductivity determinations, and is analogous to that stated on p. 293 for the chlorides of chromium. There is thus the following series:

$$[Cr_2(H_2O)_6](SO_4)_3, \text{ aq.} \quad [Cr_2(H_2O)_4SO_4](SO_4)_2, \text{ aq.} \quad [Cr_2(H_2O)_2(SO_4)_2]SO_4, \text{ aq.,}$$
$$\text{Violet.} \qquad\qquad\qquad \text{Green.} \qquad\qquad\qquad \text{Green.}$$

of which the end member is probably the completely insoluble salt, $[Cr_2(SO_4)_3]$, aq. On complete dehydration, a peach-blossom coloured sulphate, $Cr_2(SO_4)_3$, is formed, which is quite insoluble in water. If the series is continued by introducing still more SO_4 radicals into the

[1] Stortenbeker, *Rec. trav. chim.*, 1902, 21, 400.
[2] Sidgwick and Lewis, *J. Chem. Soc.*, 1926, 1287.

nucleus, the ion containing chromium becomes the anion, and double salts are formed, *e.g.* :

$$M_2[Cr_2(SO_4)_4], aq. \qquad i.e. \qquad M_2SO_4,Cr_2(SO_4)_3, aq.$$
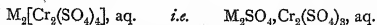
In aqueous solution none of the stages mentioned is completely stable, but an equilibrium is gradually established between the various forms. For this reason the reactions of fresh and stale solutions of chromium sulphate are different; similar behaviour has already been noted in the chlorides of chromium (p. 293).

A "chromsulphuric acid" is thus the basis of the double salts. The series may be continued further, giving the following chromsulphuric acids[1] :

$$H_2[Cr_2(SO_4)_4], aq., i.e. Cr_2(SO_4)_3 \cdot H_2SO_4, aq.,$$
$$H_4[Cr_2(SO_4)_5], aq., i.e. Cr_2(SO_4)_3 \cdot 2H_2SO_4, aq.,$$
$$H_6[Cr_2(SO_4)_6], aq., i.e. Cr_2(SO_4)_3 \cdot 3H_2SO_4, aq.$$
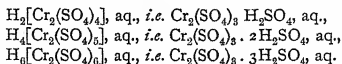
The electrical conductivity of the compounds is in agreement with the constitutional formulae given; in freshly prepared dilute solution they all fail to show the reactions either of sulphuric acid or of chromium; but after some time these reactions are obtained because the complex is not strong. In these compounds the SO_4 residue may also be replaced by the CrO_4 residue. The free acids are green; but there are compounds with an equivalent chromium and SO_4 content which are violet, and thus obviously still contain water in the nucleus. One of them, of the formula $Cr_2(SO_4)_3 \cdot H_2SO_4$, crystallises with 16 and with 24 mols. H_2O. The peach-blossom coloured compound $2Cr_2(SO_4)_3 \cdot H_2SO_4$ is an anhydrous compound altogether insoluble in water, formed by heating chromium sulphate with concentrated sulphuric acid. Its insolubility recalls that of anhydrous chromium chloride.

Other sulphates often behave in a manner similar to that described for chromium sulphate, *e.g.* titanium sulphuric acids are known. Again, ordinary ferric sulphate is brown but iron alum is pale violet; the presence of ferric salts reduces the sensitiveness of the ordinary sulphate test owing to the formation of sulphato-ferric acid. The limiting concentration is five times higher than that in iron-free solutions. The following compounds are salts of typical sulphato-acids:

$$K_3[Ir(SO_4)_3] \qquad K_4[Ce(SO_4)_4] \qquad K_4[Th(SO_4)_4].$$
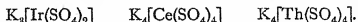
The compound $[Th(SO_4)_6]K_8$ is of interest as it shows especially clearly that the SO_4 radical, in spite of its valency of 2, sometimes takes up only one position of co-ordination (*cf.* p. 289). Ceric ammonium sulphate, $Ce(SO_4)_2 \cdot 3(NH_4)_2SO_4$, is similar to this compound (*cf.* p. 433), and sulphato-acids are frequently found in the rare earths.

Alums and Schönites.—As the valency of the central atom decreases

[1] Recoura, *Ann. chim. phys.*, 1895 (7), 4, 494 ; *Bull. Soc. chim.*, 1892 (3), 7, 200.

the complex becomes less stable, and for this reason it is difficult to prove the complex structure of the exceptionally large number of double sulphates of the uni- and bi-valent metals. These salts are decomposed in solution into their components to a large extent; the solution has properties which are obtained additively from the individual components. This even occurs in solutions of the alums, *e.g.* the conductivity of potassium aluminium alum is equal to that which would be given by an uncombined mixture of potassium and aluminium sulphates.

The *alums* form a very characteristic group of double sulphates. They have the formula $M^I[M^{III}(SO_4)_2]$, $12H_2O$.

The M^{III} in it may be many tervalent metals, such as Al, Cr, Fe, Co, Rh, Ir, Mn, V, but not Bi, Tl or the rare earths.[1] M^I may be any of a large number of univalent metals, *e.g.* K, Na, Rb, Cs, NH_4, Tl, Li,[2] the hydrazinium and hydroxylaminium radicals, but not Ag, Hg or Cu. Also, the sulphur in the alums may be replaced by selenium, *e.g.*:

$$KAl(SO_4)_2, \; 12H_2O$$
Potassium aluminium alum.

$$NaCr(SO_4)_2, \; 12H_2O$$
Sodium chromium alum.

$$(NH_4)Fe(SO_4)_2, \; 12H_2O$$
Ammonium iron alum.

$$KAl(SeO_4)_2, \; 12H_2O.$$
Selenium alum.

All alums crystallise in the regular form, mainly in octahedra, which may grow to large size. By the addition of various substances to the solution (urea, borax) the growth of the octahedral faces may be so repressed that cubical faces or others of the regular system are formed. A content of 12 mols. water is absolutely necessary for the formation of alums. Observations of the crystal lattice,[3] using Bragg's method (p. 15), have shown that the atomic skeleton would lose its stability in the absence of water; the water obviously serves to complete molecules which would otherwise be fragmentary. When this "packing water" is present the crystalline form is often extraordinarily regular, since the packing may be completed in the most favourable way in a regular structure. Even in the complicated heteropolyacids (p. 500) this regularity in external form is found, though the packing consists of molecules other than water, *e.g.* MoO_3 molecules.

Potassium aluminium alum is the prototype of the alums. It is obtained fairly easily from a solution of its components, as it is sparingly soluble. The solubility of the series of alkali alums decreases from sodium to caesium alum, so that caesium alum, owing to its low solubility, was formerly used to isolate caesium from mixtures with other alkali metals. The following serve as examples of the solubility

---

[1] The double sulphates M^I Ti^{III} $(SO_4)_2$ never contain more than $4H_2O$. Mouseron and Gravier, *Bull. Soc. chim.*, 1932, IV, 51, 1382, were unable to prepare Ti^{III} alums previously described.

[2] Spencer and Oddie, *Nature*, 1936, 138, 169.

[3] Vegard and Schjelderup, *Ann. Phys.*, 1918 (4), 54, 146.

of the alums; 100 g. water dissolve the following quantities of the anhydrous salts:

Temperature	.	.	0°	30°	60°	Melting point	
$KAl(SO_4)_2$	.	.	2·87	7·74	19·85	(92·5°)	54·45
$NH_4Al(SO_4)_2$	.	.	2·53	8·34	17·40	(95°)	52·20
$RbAl(SO_4)_2$	.	.	0·71	2·12	6·89	(109°)	58·5
$CsAl(SO_4)_2$	.	.	0·21	0·60	1·96	(122°)	62·0

The melting point is at the same time the transition point of the alum. It may be seen that this temperature rises in the direction K to Cs. The solubility of chromium alum cannot be determined, since although this deep violet substance certainly goes into solution with a violet colour, on standing, and more speedily on warming, the equilibrium mentioned on p. 582 gives some of the green form. Chrome alum also gives a green melt from which the violet form crystallises very slowly, as it does from the solution which has become green on boiling. Ferric alum is also decomposed at a much lower temperature than aluminium alum, which is the most stable of the alums. An increase in the atomic volume of the anionic metal seems to favour the stability of the anionic complex. The tendency to lose water, and thus also the vapour pressure of the water of crystallisation, rises with decreasing caesium stability. The following table gives the temperature at which some caesium alums have a vapour pressure of 300 mm.:

Anionic metal	.	.	Al	Ti	V	Cr	Fe
Atomic volume	.	.	10·2	9·3	8·8	7·7	7·1
Dissoc. temp. for 300 mm.			96·52	92	85	84	76·5°

A few salts of the alum form have one of the sulphates replaced by other compounds, e.g.

$$K_2BeF_4 . Al_2(SO_4)_3 . 24H_2O \text{ and } K_2ZnCl_4 . Al_2(SO_4)_3 . 24H_2O.$$
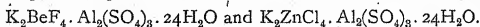
The *schönites* (double sulphates of the ferrous ammonium sulphate type) are a group which are comparable with the alums in many respects. They have the formula $M^I_2M^{II}(SO_4)_2 . 6H_2O$. The prototype is potassium magnesium sulphate $K_2Mg(SO_4)_2 . 6H_2O$. Here again the potassium atoms are replaceable by the univalent metals which occur in the alums, and the magnesium by various bivalent metals such as Zn, Ni, Co, Fe, Cu, Mn, V. Mohr's salt, $(NH_4)_2SO_4$, $FeSO_4$, $6H_2O$, is a well-known schönite. The schönites all form isomorphous monoclinic crystals. All schönites grow in saturated solutions of other schönites on evaporation and form the nucleus of the enlarged crystal; from mixtures of different schönites mixed crystals in almost any proportion separate from solution. The same phenomenon occurs with the alums. As a great variety of schönites can be prepared, they have been made use of in the study of the effect of replacing atoms in a crystal lattice by other similar atoms. To quote one result, it was found that in the formation of such analogous compounds

from their elements, the percentage contraction is always similar; but it is greater the more stable the compound. The percentage contraction in the formation from the individual components is as follows:

DOUBLE SULPHATES OF THE TYPE $M_2^I M^{II}(SO_4)_2 . 6H_2O$

	Mg	Ni	Co	Fe	Cu	Mn	Zn	Cd
K . .	44·9	44·1	43·9	43·3	43·6	...	44·2	42·8%
Rb . .	45·3	44·2	44·4	43·9	44·4	43·4	44·8	...
Cs . .	46·1	46·0	45·4	44·8	45·4	43·8	45·9	43·4%

In aqueous solution the decomposition of the schönites is just as complete as that of the alums. They are moderately soluble in water.

Sulphuric acid shows very little tendency to form heteropolyacids, although there are some salts which may be considered as derived from these acids. To these belong the double compounds $KHSO_4 . KNO_3$ and "sulphate saltpetre," $2NH_4NO_3$, $(NH_4)_2SO_4$, which are used as fertilisers. The unexpected explosive power of sulphate saltpetre recalls the destruction of parts of the Badische Anilin-u. Sodafabrik at Oppau in 1921.

Pyrosulphuric Acid, $H_2S_2O_7$.—This acid may be regarded as a complex compound formed by the elimination of 1 mol. of water from 2 mols. of sulphuric acid: $2H_2SO_4 - H_2O \longrightarrow H_2S_2O_7$. It would then have the constitutional formula indicated, but the acid gives off SO_3 very easily—a fact not in good agreement with this formula.

Pyrosulphuric acid is formed by passing SO_3 into the calculated quantity of H_2SO_4. (For the absorption of SO_3 by H_2SO_4, cf. p. 568.) The acid was previously obtained by dry heat from oxidised iron vitriol, which was thereby decomposed into SO_3, water and Fe_2O_3. Salts of this acid can be prepared by heating bisulphates: $2 NaHSO_4 \longrightarrow Na_2S_2O_7 + H_2O$.

Sulphur trioxide dissolves in sulphuric acid in all proportions. The solutions tend to lose SO_3, and therefore fume very strongly in air. Sulphuric acid with a moderate SO_3 content has a lower melting point than the pure acid; it falls from about 10° to a little below 0° when there is about 25 per cent. free SO_3 in the mixture. There is a eutectic point at this composition; if more SO_3 is added, the temperature of solidification rises and shows a maximum at the mixture corresponding to the formula $H_2S_2O_7$, when the pyrosulphuric acid is sharply indicated as a definite substance. If the SO_3 content is further increased the melting point again falls, and reaches a new eutectic point at a little above 0°, corresponding to about 65 per cent. free SO_3; it rises again on the further addition of SO_3 to the melting point of the pure oxide. Fuming sulphuric acid (*oleum*) is thus liquid when the SO_3 content is large and when it is small, but solid when the SO_3 content is medium. These relations are shown in Fig. 57, p. 573. An estimation of the

density, again, does not indicate the percentage content of SO_8, for it reaches a maximum near the composition $H_2S_2O_7$ (1·997) and falls on both sides, so that two concentrations correspond to each lower density. On the other hand, the vapour pressure of the SO_8 in oleum rises continuously with the SO_8 content. If the acid is heated, SO_8 distils and H_2SO_4 of 98·3 per cent. (cf. p. 574) finally remains, which can then be distilled at constant temperature.

Pyrosulphuric acid behaves like a mixture of H_2SO_4 and SO_8 when added to water, and the evolution of heat is accordingly very large.

Its salts are obtained by heating the bisulphate (cf. above), by heating the neutral sulphate with free SO_8 in a closed tube, or by recrystallising the sulphate or bisulphate from warm concentrated sulphuric acid. Most of the pyrosulphates easily give the bisulphate again with water, which indicates that there are but few unruptured S_2O_7 ions in solution. The alkali pyrosulphates are the best known; they dissolve very easily, and give up the excess SO_8 on calcining to a fairly high temperature. They melt much more easily than the sulphates (below red heat) and solidify in crystals from the melt. Alkaline earth and magnesium pyrosulphates are also known; the barium salt, which is obtained by recrystallising $BaSO_4$ from fuming sulphuric acid, gives off SO_8 above 400°. Very little is known of the pyrosulphates of the heavy metals; the silver salt formed from SO_8 and Ag_2SO_4 melts without decomposition. The pyrosulphates of potassium, rubidium and caesium (but not those of sodium and the alkaline earths) take up six more molecules of the acid oxide in liquid SO_8, and form crystalline compounds of the formula [1] $M_2O, 8SO_8$.

The sulphoselenic acids are closely related to the pyrosulphuric acids, and $H_2\left[O\genfrac{}{}{0pt}{}{(SO_3)}{(SeO_3)}\right]$ and $H_2\left[O\genfrac{}{}{0pt}{}{(SO_3)_2}{(SeO_3)}\right]$ can be shown to exist by the method of thermal analysis. On the other hand, the acid containing CrO_3, $H_2\left[O\genfrac{}{}{0pt}{}{(SO_3)}{(CrO_3)}\right]$ and the selenium compound $H_2\left[O\genfrac{}{}{0pt}{}{(SeO_3)}{(CrO_3)}\right]$ are both orange-coloured powders which can be obtained in the solid state as well as in the form of salts. The compound $H_2\left[O\genfrac{}{}{0pt}{}{(SO_3)}{(MoO_3)_2}\right]$, containing molybdenum, is also connected with them.

Selenic Acid, H_2SeO_4.—Selenic acid, in contrast to telluric acid, is very similar to sulphuric acid in many respects. Since selenates are rare in nature, the acid is obtained by oxidising elementary selenium, selenious acid or selenites in acid solution. Free selenium is best oxidised, first to selenious acid with nitric acid, and then to selenic acid by chloric acid. In acid solution, chlorine does not oxidise selenious acid, since the hydrochloric acid formed reduces selenic acid, though it can be carried out in alkaline solution. Oxidation by chromic acid

[1] Weber, Ber., 1884, 17, 2498.

and by lead or manganese dioxides proceeds less smoothly in acid solution. If neutral alkali selenite solutions are electrolysed with a platinum cathode, elementary selenium is immediately deposited on it as a beautiful red film. This serves as a diaphragm to separate the reducing from the oxidising portions of the cell. As the reducing area soon becomes poor in selenite, only hydrogen separates there, while at the anode oxidation to the selenate takes place smoothly. The end-point is reached when a sample liberates no iodine from acidified potassium iodide solution, since selenite oxidises potassium iodide more easily than selenate, just as nitrites have a stronger oxidising effect than nitrates. Selenium compounds containing less oxygen can also easily be converted into the sexavalent form by fusion with alkali nitrate.

Selenic acid is obtained in the form of white crystals, iso-morphous with those of sulphuric acid, by cooling highly concentrated solutions *in vacuo*. H_2SeO_4 melts at 58°, and a hydrate H_2SeO_4, H_2O (analogous to that of sulphuric acid), melts at 28°. A tetrahydrate also appears to exist. All these substances, like sulphuric acid hydrates, tend to be superfused to a very high degree; a little water lowers the melting point very notably. The density of the anhydrous liquid is 2·6, and of the solid, 3·0. It is thus denser than sulphuric acid ($d=1·84$). It is also less volatile than the latter, and at 210° has a vapour pressure of only 37 mm. On heating, the aqueous solution behaves like that of sulphuric acid: water distils off first, until a very high concentration is reached (about 97 per cent.); on further heating, dilute selenic acid first distils; the vapour becomes richer in selenic acid with rising temperature, but when the temperature rises above 260° the residue decomposes, depositing selenium dioxide and evolving oxygen. If the distillation is carried out at atmospheric pressure, the distillate below 205° is almost pure water. Selenic acid is as hygroscopic as sulphuric acid and carbonises paper and wood. It dissolves some non-metals to form colloidal solutions; *e.g.* sulphur gives a blue, selenium a green, tellurium a purple-red and iodine a brown colour; it thus resembles sulphuric anhydride.

Selenic acid can be reduced more easily than sulphuric acid. On boiling with hydrochloric acid it is rapidly converted into selenious acid, $H_2SeO_4+2HCl \longrightarrow H_2SeO_3+Cl_2+H_2O$, and it is similarly reduced by hydrogen bromide; hydrazine reduces it to elementary selenium. These reactions are important in the quantitative estimation of selenium.

The strength of selenic acid is very similar to that of sulphuric acid. Thus the heat of neutralisation with caustic potash is 31·4 Cals. for the former and 31·3 Cals. for the latter. Selenates and sulphates are isomorphous with each other and yield mixed crystals in any proportion, but the selenates sometimes contain less water of crystallisation. The double salts formed are also similar, and alums and schönites are also formed by selenic acid. The salts resemble each

other in solubility: the selenates of barium, strontium, calcium and lead are distinguished by their sparing solubility; barium selenate is a little more soluble than the sulphate, but it dissolves on being boiled with hydrochloric acid, for it is reduced to selenious acid. The salts may be obtained crystalline by fusing alkali selenates with metallic chlorides, for selenates, like sulphates, are fairly stable to heat.

Telluric Acid.—Telluric acid is quite different from selenic and sulphuric acids. It tends to form very complex isopolyacids (p. 510); the polyacid sulphates are only slightly complex, but telluric acid is in many respects more similar to iodic acid, periodic acid, tungstic acid, etc. (see p. 382). Two types of telluric acids may be distinguished: those which are beyond doubt isopolyacids and those which appear to have a simpler structure. The latter will be considered first.

The formula of ordinary telluric acid is not H_2TeO_4 but H_6TeO_6. By heating H_6TeO_6 a fine white powder is obtained which becomes yellow on heating and to which the formula H_2TeO_4 is given, but this hydrate is not characteristic. The acid H_6TeO_6 and its salts are obtained by methods similar to those used for selenic acid: by heating elementary tellurium with a mixture of nitric acid and lead dioxide, or H_2O_2,[1] or better by boiling with chloric acid. The salts can be obtained by boiling with alkaline H_2O_2, or by fusion with alkali nitrate or chlorate. Tellurites can also be used for the preparation. The acid H_6TeO_6 may be obtained by evaporating the aqueous solution at room temperature (not by heating; cf. below). It is dimorphic, usually monoclinic ($d = 3 \cdot 0$), and in contrast to sulphuric acid is not hygroscopic, though easily soluble in water. The content of a saturated solution. (H_2TeO_4), is 25·7 per cent. at 0° and 60·8 per cent. at 100°. Even at 100° solid H_6TeO_6 gives off no water, so that it is not merely H_2TeO_4 containing water of crystallisation. It is noteworthy that H_6TeO_6 is a very weak acid, about as strong as hydrocyanic acid, thus standing in complete contrast to sulphuric and selenic acids, while the glassy form of telluric acid considered below has very pronounced acidic properties. It forms an ester $Te(OCH_3)_6$.

A higher hydrate of the acid, H_6TeO_6, $4H_2O$, exists in the cold, forming large crystals which are more soluble than H_6TeO_6; the solubility curves of the two acids meet at 10°.

The other form of telluric acid, which is an isopolyacid, is formed on warming. It is colloidal and apparently varies in appearance according to the dispersity; it is, however, more likely that various polytelluric acids are formed. An insoluble form is obtained by evaporating the solution of the above acid by warming. The solution thereby becomes milky white and the residue a glassy solid, though flocks sometimes separate. This acid is very sparingly soluble in water. It is, however, a labile form, and is gradually converted into the first

[1] Gilbertson, *J. Amer. Chem. Soc.*, 1933, 55, 1460.

form; in the cold the conversion often takes weeks, but it goes more quickly on heating. Allotelluric acid has obviously quite different properties, and is formed by warming supersaturated solutions of the normal acid or on fusing the crystals. In the cold it is a sticky mass, and on heating a thin syrup is formed which is miscible with water in all proportions, and is thus probably a very highly dispersed colloid. This form also becomes slowly converted into the stable H_6TeO_6. Its reactions are radically different from those of H_6TeO_6; there is a greater difference than between metatungstic and tungstic acids. Above all, it is a really strong acid, and is therefore a stable complex, for complex formation raises the acid strength. Allotelluric acid, like many complex acids (p. 508), gives precipitates with solutions of albumin and with guanidinium carbonate: with alkalis it yields sparingly soluble precipitates, while the alkali salts of normal telluric acid are easily soluble.

The normal tellurates are derived from the weak acid, as may be seen from the alkaline reaction of even the primary acid salts, $MHTeO_4$. Besides these primary salts there are secondary tellurates of formula M_2TeO_4, aq., all of which contain at least two molecules of water, and may therefore be considered to have the composition $M_2H_4TeO_6$. All the alkali metals, together with silver and univalent mercury, give these salts: those of the alkalis dissolve easily, those of the alkaline earths are sparingly soluble, and those of the heavy metals are insoluble. They are rarely isomorphous with the sulphates (except, e.g., $RbHSO_4$ and $RbHSeO_4$), and this acid gives no tellurate alums or schönites. On the other hand, potassium tellurate is isomorphous with potassium osmate.

If the colourless salts of the formula $M_2H_4TeO_6$ are heated, yellow residues are obtained, which are derived from the salt type $M_2Te_4O_{13}$. Salts of the type M_4TeO_5 have also been described.

Telluric acid is easily reduced. On calcining, it decomposes into TeO_2, H_2O and O; its salts are much more stable to heat. In addition, like selenic acid, it is readily reduced to TeO_2 by hydrochloric acid; sulphuric acid reduces it to elementary tellurium, and with H_3PO_2 or hydrazine the separation of tellurium is quantitative.

The Persulphuric Acids

Permonosulphuric acid (Caro's acid), H_2SO_5, and **Perdisulphuric acid**, $H_2S_2O_8$, are derived from hydrogen peroxide, just as sulphuric acid and pyrosulphuric acid are derived from water. Thus permonosulphuric acid (Caro's acid) (I.) may be considered to be formed by the substitution of one hydrogen atom in HOOH, and perdisulphuric acid (II.) by substituting both hydrogen atoms.

I. $HSO_3 - OOH.$ II. $HSO_3 - OO - SO_3H.$
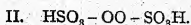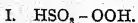
The pure acids are prepared by double decomposition between chlorsulphonic acid and anhydrous H_2O_2:

I. $HSO_2 - Cl + HOOH \longrightarrow HSO_3 - OOH + HCl$.
II. $2 HSO_3 - Cl + HOOH \longrightarrow HSO_3 - OO - SO_3H + 2 HCl$.
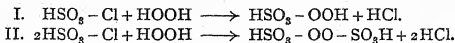
These reactions take place with a slight evolution of heat, and the reaction mixture remains liquid at first but solidifies in time, especially in the cold, depositing crystals of the acid.[1]

Another method of preparation involves the electrolysis of aqueous sulphuric acid, when both per-acids are formed (cf. below). The reaction does not consist merely in the withdrawal of the charge from the ions HSO'_4, but the oxygen evolved at the anode or the H_2O_2 formed plays an active part, so that the reaction can be shown by the equation

$$2 HSO'_4 + O + H_2O \longrightarrow H_2S_2O_8 + 2 OH'.$$
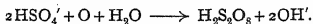
The yield of $H_2S_2O_8$ is appreciably influenced by the potential difference at the electrode, although even if the P.D. were not favourable the HSO'_4 ions would be still discharged and give the material for the formation of $H_2S_2O_8$, according to the scheme of polymerisation. The per-acid, however, is only formed to a measurable extent when there is an appreciable over-voltage at the electrodes. This is favoured by the use of smooth platinum electrodes; at an electrode covered with platinum black the over-voltage is lacking and scarcely any per-acid is formed; nor is any quantity formed at iridium electrodes. A high anode potential is obtained by the addition of chlorine or fluorine ions to the solution; the yield of per-acid is therefore especially good when some hydrochloric acid is added to the electrolyte. It is further increased by a high current density. The anode and cathode spaces must be separated, since the per-acid is again reduced at the cathode. Lowering the temperature raises the anode potential, so that the anode is cooled; otherwise, owing to the high current density which is used, the liquid would be warmed and the per-acid tend to decompose (cf. p. 592). Moreover, the choice of the correct concentration of sulphuric acid is of great importance. Increasing concentration favours per-acid formation, but a certain concentration must not be exceeded or the sulphuric acid hydrolyses the perdisulphuric acid, which is converted to Caro's acid, $H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$. The most suitable concentration is given by sulphuric acid of a density 1·42. Caro's acid, however, is formed in addition to perdisulphuric acid under all conditions; indeed, under certain experimental conditions, in a sulphuric acid of $d = 1·236$, as much as 36 per cent. is formed besides perdisulphuric acid, and in acid of $d = 1·468$, 83·2 per cent. is produced. In very concentrated acid hydrogen peroxide is also formed

[1] d'Ans and Friedrich, Z. anorg. Chem., 1912, 73, 345.

in small quantities, but below a density of 1·40 its formation is scarcely noticeable.

The yield obtained by electro-chemical oxidation also varies very considerably with the nature of the cations present. The hydrogen ion of sulphuric acid is not very favourable to the course of the reaction; nor are sodium and magnesium ions. The process proceeds much more favourably in the presence of ammonium, potassium or nickel ions. Instead of free sulphuric acid, therefore, it is better to electrolyse its potassium salt, or still better, its ammonium salt. The effect on the yield is seen from the following data:

Sulphuric acid per litre	.	8	240	400 g.
As free H_2SO_4	.	0·0	1·0	15·5% yield
Combined with NH_3	.	11·1	59·1	82·2% ,,

The potassium salt is the most sparingly soluble of all persulphates, the ammonium salt being slightly more soluble, so that these salts crystallise out and may be used direct. Technically, a solution of ammonium persulphate is usually formed first, and then decomposed with potassium sulphate. Potassium persulphate is precipitated, whilst ammonium sulphate is formed anew, and is again electrolysed. The persulphates of rubidium and caesium may be obtained in a similar way, as the solubility diminishes in a series K $\longrightarrow$ Rb $\longrightarrow$ Cs $\longrightarrow$ Tl. The barium and lead salts are easily soluble. The silver salt $Ag^{II}S_2O_8$, $4C_5H_5N$ (p. 700) is interesting.

Properties.—Both acids are crystalline; perdisulphuric acid forms only small white crystals, while Caro's acid may be obtained in splendid transparent prisms a centimetre long. The former melt at 65° with decomposition, and the latter, undecomposed, at 45°. Caro's acid, but not perdisulphuric acid, can be purified from adhering sulphuric acid by being remelted and centrifuging away the mother liquor. Both acids are extremely hygroscopic, like sulphuric acid, and hiss when poured into water. They carbonise paper, sugar and even paraffin. Caro's acid dissolves very well in alcohol and ether, perdisulphuric acid only to a limited extent. As a result of the oxidising action of the acids, they cause many organic substances to explode; *e.g.* on adding Caro's acid to benzene or phenol, or sometimes when perdisulphuric acid is shaken with ether. There is a characteristic difference between the oxidising effect of the two acids; Caro's acid, which has the hydrogen peroxide radical unprotected, oxidises hydrogen iodide instantly, and converts aniline into nitrosobenzene and nitrobenzene, while perdisulphuric acid does not give these reactions, though ferrous salts are immediately oxidised by perdisulphuric acid. Neither of these acids, however, gives those reactions of hydrogen peroxide which depend on the formation of other per-acids, and thus the yellow coloration of titanic acid, the blue coloration of chromic acid and the reduction of permanganic acid are not obtained (p. 408). They may thereby be distinguished from H_2O_2.

The acids can be kept in the solid condition if they are pure and dry. In this state Caro's acid may be kept for weeks and perdisulphuric acid for a still longer time without decomposition. Once the decomposition begins, however, it proceeds quicker and quicker, owing to the action of the decomposition products. Caro's acid may be kept in solution much better than perdisulphuric acid if a great deal of sulphuric acid is present. In concentrated sulphuric acid solution at 0°, perdisulphuric acid may be completely converted into Caro's acid within two days: $H_2S_2O_8 + H_2O \longrightarrow H_2SO_5 + H_2SO_4$. Caro's acid can therefore be conveniently obtained by dissolving a persulphate in warm concentrated sulphuric acid. Hydrogen peroxide reacts similarly :

$$H_2S_2O_8 + H_2O_2 \longrightarrow 2H_2SO_5.$$
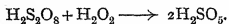
On the other hand, $H_2S_2O_8$ can be kept for days in dilute sulphuric acid without decomposition. The decomposition of Caro's acid, $H_2SO_5 + H_2O \longrightarrow H_2SO_4 + H_2O_2$, proceeds much more slowly even in concentrated sulphuric acid and is reversible, so that a certain quantity of Caro's acid may be obtained [1] from concentrated H_2SO_4 and H_2O_2. If, however, the H_2O_2 formed is distilled off, the Caro's acid is completely decomposed, since the equilibrium is disturbed; the technical preparation of 30 per cent. hydrogen peroxide is based on this reaction. In dilute solution H_2O_2 is rapidly formed from both acids on warming, so that a boiling persulphate solution acts on a metallic salt in the same way as hydrogen peroxide.

In addition to these decompositions, which depend on hydrolysis, there is a second kind, which consists in the elimination of free oxygen, $M_2S_2O_8 + H_2O \longrightarrow 2MHSO_4 + O$. The oxygen produced contains a little ozone. This decomposition is not shown so much by the alkali salts of perdisulphuric acid as by the free acid, and in the latter it is generally only noticeable above 50°. The solid alkali salts may be kept permanently at room temperature if water is absent; the barium salt, on the other hand, contains water of crystallisation, and decomposes in the course of a few weeks into a damp mass which contains perdisulphuric acid and barium sulphate.

Little is known of the salts of Caro's acid. A potassium salt is obtained according to the equation $KSO_3 . Cl + H_2O_2 \longrightarrow KSO_3 . OOH + HCl$, but only in an impure condition. An aniline salt may be prepared by precipitating the ethereal solution with aniline.

Perselenic acid is non-existent. An impure potassium perselenate was obtained by Dennis and Brown [2] by the electrolytic oxidation of potassium selenate.

Sulphur heptoxide, S_2O_7, is prepared by the action of ozonised

[1] Baeyer and Villiger, *Ber.*, 1901, 84, 856.
[2] *J. Amer. Chem. Soc.*, 1901, 23, 258.

oxygen on SO_2 or SO_3, a method due to Berthelot.[1] At o° sulphur heptoxide forms a mass of slender, elastic crystals, similar to SO_3; it has a high vapour pressure and can be sublimed. The heptoxide easily loses oxygen but can be kept for several days in the cold. It dissolves with a hissing noise in water. The oxide does not appear to be the true anhydride of persulphuric acid, for on neutralisation with bases, sulphates and oxygen are produced as well as persulphates. It is doubtful if it is a true compound; the negative heat of formation suggests that it may be a loose addition product of oxygen with sulphur trioxide, or a mixture of SO_4 and SO_3.

Sulphur Tetroxide, SO_4 or S_2O_8.—This compound is formed by the action of the silent electric discharge on a mixture of sulphur dioxide and oxygen in the proportion 1 : 10 at o·5 mm. pressure.[2] It can be distinguished from the above compound by the difference in vapour pressure. The product containing SO_4 forms matted crystals, which decompose at room temperature with liberation of oxygen and ozone and formation of S_2O_7. The fluorination of sulphuric acid[3] gives rise to a product with similar properties. It converts manganese sulphate into permanganate, phenolphthalein into fluorescein, and cannot be identified with either perdisulphuric or Caro's acid. Silver peroxide is immediately precipitated from silver nitrate solution. The SO_4 is probably formed according to the equation $H_2SO_4 + F_2 \longrightarrow 2HF + SO_4$. At the moment there is no evidence to decide between the formulae SO_4 and S_2O_8.

Halogen Derivatives of the Sulphur Acids

The following compounds may be considered to be formed by the replacement of one or two hydroxyl groups in sulphurous, sulphuric or pyrosulphuric acids by fluorine or chlorine :

SOF_2 .	. Thionyl fluoride		$SOBr_2$.	. Thionyl bromide
$SOCl_2$.	. Thionyl chloride		SOI_2 .	. Thionyl iodide
SO_2F_2 .	. Sulphuryl fluoride		SO_2Cl_2 .	. Sulphuryl chloride
HSO_3F	. Fluorsulphonic acid		HSO_3Cl .	. Chlorosulphonic acid
	$ClSO_2 . O . SO_2Cl$.	. Pyrosulphuryl chloride		

Of the selenium compounds $SeOF_2$, $SeOCl_2$ and $SeOBr_2$ are known. The tellurium compounds are oxysalts, but have no appreciable interest.

Derivatives of Sulphurous Acid.—The "thionyl" compounds SOF_2, *i.e.* $F_2S \rightarrow O$ and $SOCl_2$, *i.e.* $Cl_2S \rightarrow O$, may be regarded as derived from the symmetrical form of sulphurous acid. Thionyl fluoride is obtained by way of the chloride, which exchanges its chlorine atoms for fluorine on being heated with AsF_3 : $3SOCl_2 + 2AsF_3 \longrightarrow$

[1] Berthelot, *Compt. rend.*, 1878, **86**, 20; Schmidlin and Massini, *Ber.*, 1910, **43**, 1169.
[2] Schwarz and Achenbach, *Z. anorg. Chem.*, 1934, **219**, 271.
[3] F. Fichter and W. Bladergroen, *Helv. Chim. Acta*, 1927, **10**, 553.

$3SOF_2 + 2AsCl_3$. Thionyl chloride is obtained by replacing one of the oxygen atoms in SO_2 by chlorine, by means of PCl_5: $SO_2 + PCl_5 \longrightarrow SOCl_2 + POCl_3$. It is also obtained synthetically from sulphur and Cl_2O: $S + Cl_2O \longrightarrow SOCl_2$; but this method is less useful, as Cl_2O is difficult to handle. Both thionyl fluoride and chloride are colourless and fume slightly, as they give off halogen hydride in damp air. They have a typical sharp odour: that of the fluoride is particularly stifling and recalls that of phosgene, $COCl_2$, which is similar to it in formula, and like that compound it irritates the mucous membrane. The fluorine compound is gaseous, liquefies at $-30°$ and solidifies at $-110°$; the chlorine compound is, at normal temperatures, a highly refractive liquid, boiling at $78°$. Both substances may be vaporised without decomposition, but split up if the vapour is further heated. The decomposition of the chloride, which occurs above $154°$, takes place with formation of Cl_2, SO_2 and S_2Cl_2. The fluoride requires a still higher temperature for decomposition; it attacks glass only above $400°$. In general, thionyl fluoride is fairly inactive; e.g. it reacts with sodium only at high temperatures and is but slowly decomposed by water thus: $SOF_2 + H_2O \longrightarrow 2HF + SO_2$. Thionyl chloride undergoes this decomposition somewhat more easily; for its reactions with ammonia, cf. pp. 648, 735. It reacts with NH_4CNS in liquid SO_2 and thionyl thiocyanate, $SO(CNS)_2$ is formed [1] (see p. 549). Thionyl bromide [2] is an orange-yellow liquid formed by the action of HBr on $SOCl_2$. It boils at $138°$ (773 mm.) and freezes at $-52°$.

Thionyl iodide is prepared from thionyl chloride by the method used for sulphur iodide (p. 601).

Selenyl fluoride, $SeOF_2$, melts at $4.6°$ and boils at $124°$; selenyl chloride, $SeOCl_2$, is formed by heating $SeCl_4$ and SeO_2 in CCl_4 solution : $SeCl_4 + SeO_2 \longrightarrow 2SeOCl_2$. It forms an almost colourless liquid, which solidifies at $8.5°$ to pale yellow crystals, and boils at $176.4°$. It dissolves in chloroform without decomposition, and sulphur, selenium, tellurium, bromine and iodine are readily soluble in it. It also dissolves bakelite, gums, celluloid and glue. Many unsaturated hydrocarbons dissolve in it, but the saturated forms are insoluble ; likewise MoO_3 is soluble and WO_3 is insoluble, and in presence of sulphuric acid, Nb_2O_5 dissolves and Ta_2O_5 is sparingly soluble. It is hydrolysed by water to selenious acid. Selenium oxybromide, $SeOBr_2$, which can be prepared from SeO_2, Se and Br, is chemically similar to the chloride. It is reddish yellow, melts at $41.5°$ and boils at $217°$ with decomposition.

Derivatives of Sulphuric Acid.—There are two classes of these halogen compounds ; in the first, only one hydroxyl group of the sulphuric acid is replaced by halogen, so that these are still acidic (fluor- and chlor-sulphonic acids), while in the second, as a result of the exchange of both hydroxyl groups, the acid properties are lost (sulphuryl fluoride and chloride ; pyrosulphuryl chloride). The acids show the decrease

[1] Jander and Ullmann, *Z. anorg. Chem.*, 1937, 230, 405.
[2] Partington and Mayer, *J. Chem. Soc.*, 1926, 129, 2594.

in stability from the fluorine compounds to those with the heavier halogens exceptionally well.

Fluorsulphonic acid, HSO_3F, is by far the most stable, and even in water is only partially decomposed with the formation of sulphuric acid. An equilibrium is set up—$HSO_3F + H_2O \rightleftharpoons H_2SO_4 + HF$—which, when 1 part acid and 1·2 parts of water are used, yields about 1·4 per cent. sulphuric acid, and even when 51 parts of water are used to 1 part of acid there is still 70 per cent. of the acid unchanged. Fluorsulphonic acid is therefore also formed from hydrofluoric and sulphuric acids, and it is present in large quantities in a mixture of them as prepared from calcium fluoride and sulphuric acid. It can be obtained by distilling this mixture. It is also formed when hydrofluoric acid comes into contact with sulphur trioxide: $SO_3 + HF \longrightarrow HSO_3F$. The potassium salt is also obtained from potassium pyrosulphate, which contains labile SO_3: $K_2S_2O_7 + KF \longrightarrow KSO_3F + K_2SO_4$.

Free fluorsulphonic acid is a mobile, colourless liquid which fumes in air and is decomposed by water, to yield the equilibrium mixture mentioned above. It dissolves in nitrobenzene without decomposition. It boils at 162·6°, and on distillation undergoes decomposition into SO_2F_2 and H_2SO_4 to a slight extent. The barium salt decomposes much more smoothly, so that it is employed in the preparation of SO_2F_2, but the alkali salts are exceptionally stable to heat. They are obtained by warming a solution of the ammonium salt with alkali hydroxide, a method which indicates the great stability of these salts in alkaline solution. They can be recrystallised from neutral solution, and even on boiling they decompose only very slowly. They are more easily decomposed after the addition of free mineral acid. The conversion of this acid into amidosulphonic acid by ammonia (p. 639) is an important reaction.

The known salts of this acid are all easily soluble in water; the solubility of the barium salt permits any admixed sulphuric acid to be very easily separated. Silver, lead and copper salts also give no precipitates with solutions of its alkali salt. The organic base "nitron" (*cf.* p. 695) alone gives a sparingly soluble salt. The alkali salts are anhydrous and stable in air, even the deliquescent sodium salt. The lithium compound crystallises with 3 mols. H_2O.

Chlorsulphonic acid, HSO_3Cl, may be hydrolysed much more easily. For this reason it can only be obtained in the absence of water; *e.g.* synthetically: $SO_3 + HCl \longrightarrow HSO_3Cl$, for which it is unnecessary to employ free SO_3, but is sufficient to use its solution in sulphuric acid (fuming sulphuric acid). Alternatively, PCl_5 may be added to fuming sulphuric acid; or the chlorsulphonic acid can be made by a partial hydrolysis of sulphuryl chloride, $SO_2Cl_2 + H_2O \longrightarrow SO_2(OH)Cl + HCl$.

The acid is a colourless liquid, boiling point, 150°. It partly decomposes into its components, HCl and SO_3, on boiling. It fumes

energetically in air and is decomposed by water with exceptional violence. The salts of this acid, which would correspond to the chlor-chromates (p. 483), have not been prepared.

Neither a brom- nor an iodo-sulphonic acid is known, nor are sulphuryl bromide or iodide.

Sulphuryl chloride and fluoride, SO_2Cl_2 and SO_2F_2, may also be regarded as addition products of halogen and SO_2. They are actually formed by the union of these substances, but the reaction $SO_2 + Cl_2 \longrightarrow SO_2Cl_2$ is only completed directly when the liquefied gases or concentrated solutions are used; e.g. they are brought together in the presence of camphor, which has a solvent power for SO_2 exceeding that of all other media. Sunlight accelerates the reaction in an extraordinary way and active carbon is now used as a catalyst. The combination of fluorine and sulphur dioxide is only completed after it has been induced by means of a glowing platinum wire. There is also a special reaction for the preparation of these compounds: the fluoride is formed very readily by the action of heat on dry barium fluorsulphonate, $Ba(SO_3F)_2 \longrightarrow BaSO_4 + SO_2F_2$, and the chloride is formed at $70°$ from chlorsulphonic acid, $2SO_2(OH)Cl \longrightarrow SO_2Cl_2 + H_2SO_4$, with the aid of accelerators (Sb, Sn or Hg).

Both compounds are very stable in the dry condition and decompose only at a red heat. Sulphuryl chloride sinks in water, and then remains almost unchanged in the cold for some time. Sulphuryl fluoride is not attacked by water even at $150°$; at room temperature it dissolves in about ten volumes of water. Both compounds dissolve in indifferent liquids, such as chloroform; alcohol takes up 3 vols. SO_2F_2. They react violently with ammonia (cf. p. 647). Sodium, even when molten, has no effect on sulphuryl fluoride. Sulphuryl chloride is a colourless liquid with a piercing odour, which boils at $70°$; sulphuryl fluoride is a colourless gas which liquefies at $-52°$ and solidifies at $-120°$.

No true halogenated selenic acid is known. The salt $(NH_4)_2SeO_4$, HF, approximates to one, and crystallises from an aqueous solution of its components; it may be regarded as $\left[SeF \begin{matrix} O_3 \\ OH \end{matrix} \right] (NH_4)_2$.

Pyrosulphuryl chloride, $ClSO_2 . O . SO_2Cl$, may be regarded either as the dichloride of pyrosulphuric acid, or as the anhydride of chlor-sulphonic acid. This compound forms a colourless thick liquid, which solidifies at $-39°$ and boils at $145°$. Its vapour undergoes decomposition at higher temperatures: $S_2O_5 . Cl_2 \longrightarrow SO_2 + SO_3 + Cl_2$. Pyro-sulphuryl chloride sinks in water as an oil and is hydrolysed only after some hours; consequently it does not fume strongly in air. It is formed on dehydrating chlorsulphonic acid by means of P_2O_5, and

also according to the equation $2SO_3 + PCl_5 \longrightarrow POCl_3 + S_2O_5Cl_2$. It is also formed when SO_3 is dissolved in cold S_2Cl_2 and the solution warmed; SO_2 then escapes and pyrosulphuryl chloride remains behind.

Halogen Compounds of Sulphur, Selenium and Tellurium

Sulphur, selenium and tellurium form the following halogen compounds (for thiocyanates, *cf.* p. 603):

SF_6	S_2F_{10}	SF_4	SF_2	S_2F_2	SeF_6	...	SeF_4	TeF_6	$TeF_4(?)$
...	S_2Cl_4	SCl_4	SCl_2	S_2Cl_2	$SeCl_4$	$SeCl_2$*	Se_2Cl_2	$TeCl_4$	$TeCl_2$
...	...	...	...	S_2Br_2	$SeBr_4$	...	Se_2Br_2	$TeBr_4$	$TeBr_2$
...	...	...	...	S_2I_2	...	...	Se_nI_2	TeI_4	...

Only in the gaseous form in presence of chlorine.

Preparation.—These compounds are all prepared by direct union of the components; *e.g.* SF_6 is obtained by passing fluorine over sulphur, and S_2Cl_2 when sulphur and gaseous chlorine react. This method of preparation does not fail for any of these compounds except possibly for S_2F_2, which can be made by heating silver fluoride or mercurous fluoride with sulphur: $2AgF + 3S \longrightarrow Ag_2S + S_2F_2$. S_2F_{10} is formed[1] in small yield simultaneously with SF_6. S_2F_2 and SF_2 have not been prepared pure, and SF_4 was obtained[2] by the interaction of CoF_3 and S. If there are several compounds of the same components, as SCl_4 and S_2Cl_2, then the one or the other is formed according to whether an excess of halogen or of sulphur is used, and by subsequent addition of one component the compound may be altered; *e.g.* $SCl_4 + 3S \longrightarrow 2S_2Cl_2$. The formation of these compounds takes place only after an induction period unless catalysts such as $SbCl_5$ or I_2 are present, and the reactions occur most readily on cooling to $-75°$, *e.g.* for the formation of SCl_2 and SCl_4. In consequence of the metastable condition of a fresh mixture of Cl_2 and S_2Cl_2 the existence of SCl_2 was doubted until recently, as the physico-chemical measurements were made on uncombined mixtures. It is unnecessary for the halogen to be used in the elementary condition; *e.g.* if sulphur and phosphorus pentachloride are heated, sulphur chloride and phosphorus trichloride are formed; the same result is obtained when metallic sulphides are used instead of sulphur.

The tellurium halides, in contrast to those of sulphur and selenium, may be prepared and kept in the presence of water (TeF_6 is an exception; *cf.* p. 602). Thus TeI_4 is not only obtained by rubbing the

[1] Denbigh and Whytlaw-Gray, *J. Chem. Soc.*, 1934, 1347.
[2] Ruff and Ascher, *Z. anorg. Chem.*, 1929, **183**, 193; Ruff, *Ber.*, 1936, 69A, 181.

elements together under water, but also by double decomposition of the dioxide with hydriodic acid:

$$TeO_2 + 4HI \rightleftharpoons TeI_4 + 2H_2O;$$
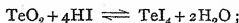
but this reaction leads to a definite equilibrium. Tellurium dibromide decomposes both in the gaseous form and in solution:

$$2TeBr_2 \rightleftharpoons TeBr_4 + Te.$$
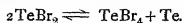
Properties.—The hexafluorides of this group are colourless gases, and solidify at low temperatures to white crystalline masses, without previously forming liquids. S_2F_{10} boils at $29°$ and melts at $-92°$. S_2F_2 is also a colourless gas, with a remarkably small range of existence as a liquid—from $-105.5°$ to $-99°$. Selenium tetrafluoride is a colourless liquid, and selenium and tellurium tetrachlorides form white crystals; other compounds are coloured:

S_2Cl_2	. Light yellow.	$TeCl_2$.	. Black, vapour dirty red.
SCl_2 .	. Red.	$TeBr_2$.	. Chocolate brown, vapour
S_2Br_2	. Red.		deep violet.
$SeCl_2$	. Brownish yellow.	$TeBr_4$.	. Reddish yellow.
Se_2Br_2	. Deep blood-red.	TeI_4 .	. Iron grey.
$SeBr_4$	. Orange red.	$TeBr_2I_2$.	. Ruby-red crystals.

It is possible to obtain the melting points of some of these compounds; *e.g.*:

S_2F_2	S_2Cl_2	SCl_4	S_2Br_2	SeF_4	$TeCl_2$	$TeCl_4$	$TeBr_2$	$TeBr_4$
$-105.5°$	$-80°$	$-31°$	$-46°$	$-13°$	$175°$	$214°$	$210°$	$380°$

Some of these substances sublime undecomposed (before melting) at the following temperatures: TeF_6, $-36°$; $SeCl_4$, $<200°$. SF_6 melts at $-50.5°$ and sublimes at $-63.8°$.

Besides the hexafluorides and S_2F_{10}, the compounds S_2F_2 (b.pt. $-99°$), S_2Cl_2 (b.pt. $138°$), $TeCl_2$ (b.pt. $324°$), $TeCl_4$ (b.pt. $380°$), $TeBr_2$ (b.pt. $339°$) and SeF_4 (b.pt. $93°$) may be gasified without decomposition. In the state of vapour S_2Cl_2 gives indications of polymerisation, though in solution it has a simple molecular weight. All the others are split up on vaporisation. S_2Br_2 may be distilled under reduced pressure—*e.g.* at $54°$ at 0.18 mm.—but it decomposes on heating under atmospheric pressure, when the residue gives a distillate richer in bromine as the temperature rises. This decomposition begins at $60°$. Se_2Br_2 and Se_2Cl_2 behave similarly, and begin to give off orange-coloured vapours at about $100°$, whereupon the boiling point rises and decomposition into $SeCl_4$ and Se occurs. $SeBr_4$ may be sublimed with only partial decomposition. The thermal decomposition of SCl_4 has been most carefully studied; if S_2Cl_2 is gradually saturated with chlorine, the solutions formed have at first properties which change continuously with variation in their chlorine

content; when represented graphically they show no break or transition point at the composition SCl_2. Thus the melting point curve only shows maxima at the compositions SCl_4 and S_2Cl_2, and the chlorine content of the vapour rises quite regularly with increase in the chlorine content of the liquid. The darkening of the colour of the liquid when the composition SCl_2 is reached points to the existence of this substance; and if one waits a long time or cools the mixture to $-90°$ or adds a catalyst, the melting point curve not only gives unmistakable evidence of the existence of SCl_2 but also of the otherwise unknown compound S_3Cl_4. Measurements of surface tension, density, dielectric constant, and especially of the spectrum, show that SCl_2 is a well characterised substance of red colour, which can also be frozen out of the mixtures. In the liquid state it is partly decomposed—at $0°$ about 15 per cent. and at $100°$ about 25 per cent. is broken up. *Liquid* mixtures of sulphur and chlorine contain only the three components S_2Cl_2, SCl_2 and Cl_2; the other sulphur chlorides, SCl_4 and S_3Cl_4, appear only when the liquid is frozen and are dissociated on melting.[1] Repeated fractional distillation causes complete decomposition into S_2Cl_2 and Cl_2. The compound SCl_4 can be stabilised by the formation of labile double compounds with halogen compounds of weakly saline character, such as the trichlorides of iodine, antimony, gold, iron and aluminium, and the tetrachlorides of tin, titanium and zirconium.

Selenium tetrachloride, as may be conjectured from the behaviour of SCl_4, cannot be vaporised unchanged. Between $109°$ and $226°$ the vapour density falls to a half of its normal value, indicating complete dissociation into the dichloride and chlorine: $SeCl_4 \longrightarrow SeCl_2 + Cl_2$. The pure liquid dichloride cannot be prepared from its elements. A chlorine-selenium mixture corresponding to its formula yields the solid tetrachloride and liquid Se_2Cl_2 on freezing. Also, Se_2Cl_2, which begins to give off orange-coloured vapours at about $100°$, decomposes markedly, and cannot be distilled without decomposition. Tellurium tetrachloride boils almost without decomposition, but is split up on heating the vapour above the boiling point. Tellurium tetrabromide boils at $420°$ and then undergoes partial decomposition into the dibromide and bromine. The tetriodide also gives off iodine on heating.

The volatile compounds have a peculiar odour: that of S_2Cl_2 is piercing and sharp, but also musty and "sulphurous," and is partly due to the presence of its decomposition products in air, HCl and SO_2. Se_2Cl_2 has a very similar but less intense smell, and those of the bromide S_2Br_2, of the fluoride S_2F_2 and of Se_2Br_2 approximate to that of sulphur chloride. S_2F_2 causes great difficulty in breathing. Of the hexafluorides, TeF_6 smells like a mixture of arsine and ozone, but SF_6 is almost odourless, in accordance with its general chemical indifference.

In sulphur hexafluoride there is obviously a very complete internal

saturation of its chemical affinity. It is remarkably inert, is not decomposed by water at all, nor by alkali hydroxides, ammonia or hydrochloric acid. Metallic sodium may be fused in it without reaction setting in, decomposition only taking place when it is very strongly heated.[1] Disulphur decafluoride is somewhat less stable. In contrast to these, the unsaturated difluoride S_2F_2 is readily hydrolysed to S, SO_2, and HF, while selenium tetrafluoride, SeF_4, is decomposed by atmospheric moisture: $SeF_4 + 2H_2O \longrightarrow SeO_2 + 4HF$ —it attacks glass and fumes strongly. It is not attacked by many elements (H, S, Si, C, As, I), but reacts with the alkali metals, mercury and phosphorus. Tellurium hexafluoride is slowly decomposed by water to form telluric acid.

The chlorides and bromides of sulphur and selenium are fairly rapidly hydrolysed by water: they first sink to the bottom as oils, and then undergo decomposition. The hydrolysis of the tetrahalogen compounds may take place by a simple reaction—*e.g.* $SCl_4 + 2H_2O \longrightarrow SO_2 + 4HCl$ —but that of compounds of the type S_2Cl_2 is very complicated and no simple equation can be given for it. With the monochloride, $S_2(OH)_2$ is probably first formed, and with the dichloride, $S(OH)_2$; from these primary products sulphur, sulphur dioxide and halogen hydride are formed as chief products, but polythionic and sulphuric acids are also formed. Alkali hydroxides also hydrolyse these halides, giving similar products.[2] The decomposition of $TeCl_2$, again, is not simple, and elementary tellurium and tellurous acid are formed; $TeBr_2$ decomposes similarly into Te and $TeBr_4$. The $TeBr_4$, however, dissolves in a little water without hydrolysis and gives a yellow colour. On evaporating this solution dark ruby-red plates separate, which contain water and effloresce in air to form a yellow powder.

Sulphur monoiodide is formed by the action of dry potassium iodide on a solution of the chloride in carbon tetrachloride. It is hydrolysed in the same way as the monochloride.[3] A selenium iodide (Se_nI_2) is indicated[4] by the spectrum of mixtures of Se and I in CS_2.

The halogen compounds of tellurium resemble those of quinquevalent antimony, and tend to form double salts and to build complex halogen acids. Thus the tetrahalides of tellurium form halogen salts of the form M_2TeCl_6 (yellow), M_2TeBr_6 (dark red) and M_2TeI_6 (black), which crystallise in octahedra and resemble the platinum double halides. Of these, as in the platinum compounds, the iodides and the caesium compounds are the most sparingly soluble. If a solution of tellurium tetrahalide is saturated with halogen hydride at a low temperature, the

[1] Moissan and Lebeau, *Compt. rend.*, 1900, **30**, 1436.

[2] Holst, *Bull. Soc. chim.*, 1940, [v] **7**, 276 ; B. S. Rao, *Proc. Indian Acad. Sci.*, 1939, **10** *A.*, 423.

[3] Rao, *Proc. Indian Acad. Sci.*, 1940, **11**, A, 162, 185.

[4] McCullough, *J. Amer. Chem. Soc.* 1939, **61**, 3401.

unstable halogen acid, $HTeX_5$, $5H_2O$, crystallises. The chlorine compound is yellow and melts at $-20°$, while the orange-red needles of the bromine compound decompose at $+20°$. A part of the water in these compounds probably belongs to the complex. TeF_4 has not been obtained in the free state, but is known in the form of a hydrate with 4 mols. H_2O; this is formed at low temperatures from TeO_2 and HF, and is closely related to the halogen salts of the form $MTeF_5$.

Solubility.—Some of these compounds dissolve undecomposed in chloroform and carbon disulphide. The latter is miscible with S_2Cl_2 and Se_2Cl_2 in all proportions, while $SeCl_4$ is not soluble in it and may thereby be purified from Se_2Cl_2. $TeCl_4$ is only very slightly soluble in carbon disulphide in the cold, but much more dissolves on warming. The solubility of elementary sulphur and selenium in the halogen compounds of sulphur and selenium is very remarkable. This is best known in S_2Cl_2—the best solvent for sulphur. The condition of the sulphur in this solution is discussed on p. 125. Such solutions of sulphur find technical application in the vulcanisation of rubber. The corresponding selenium compound, Se_2Cl_2, dissolves only a little sulphur, but takes up large quantities of selenium, and Se_2Br_2 can dissolve 22 per cent. of selenium. The free halogens also dissolve in these compounds. Thus S_2Cl_2 takes up bromine and iodine freely to form liquids which conduct the electric current to a remarkable extent. It is not yet known what ions make the transport of the current possible; the dissociation of I_2 into a positive and negative iodine ion is improbable; more probably the addition of the iodine molecule to S_2Cl_2 is followed by ionisation into S_2Cl_2I ions and free I ions. Some of the halogen compounds also dissolve elementary phosphorus. S_2Cl_2 mixes with liquid sulphur dioxide in all proportions, apparently without chemical reaction. Below $0°$, S_2Cl_2 dissolves 5 molecules of gaseous sulphur dioxide, but on warming some SO_2 escapes. The halogen compounds react with metals to form metallic halides and sulphur is liberated; the alkali metals may catch fire in contact with these halides. Ammonia yields nitrogen sulphide (p. 735) with S_2Cl_2.

Constitution.—The di-, tetra- and hexa-halogen compounds of this series may be derived from bi-, quadri- and sexa-valent sulphur. The existence of sulphur hexafluoride is held to be a proof of the possible sexacovalency of sulphur, and the stability of this substance is also in accordance with this formulation. The electronic formula is therefore I, but formulae II, III, and IV containing single electron linkages

I.   II.   III.   IV.
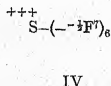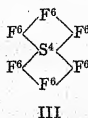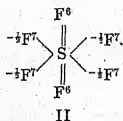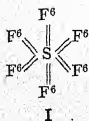
have also been suggested[1]; such singlet formulae have not found general acceptance, largely on the grounds of the instability usually associated with such linkages. The structures of SF_6, SeF_6 and TeF_6 have been studied by the electron diffraction method.[2] The molecules are regular octahedra, and the observed bond distances in each case are somewhat less than those calculated for covalent duplet linkages. The cause of this discrepancy is not clear, but it is not due to singlet linkages, for such bondings should be of greater length than duplet linkages. Similar discrepancies are met with also in PCl_3, $AsCl_3$, PF_3, AsF_3, $SiCl_4$, $GeCl_4$ and $SnCl_4$—in which the duplet formulation has never been questioned. Here, as in the sulphate ion, the shortening of the S—F bond is probably due to its partial double-bonded character.

The electronic formulæ $Cl^6=S^4=Cl^6$ and $Cl^6=S^4=S^4=Cl^6$ can be used for SCl_2 and S_2Cl_2, but Spong[3] has suggested, from its varied properties, that S_2Cl_2 is a mixture of $Cl^6=S^4=S^4=Cl^6$ and $\bar{S}^6=\overset{+}{S}^2{\displaystyle\diagdown\diagup}{\!\!\!\overset{Cl^6}{\underset{Cl^6}{}}}$,

i.e. $S \longleftarrow SCl_2$. The high dielectric constants of solid SCl_4 and S_3Cl_4 indicate that they have salt structures,[4] and may, therefore, be formulated.

$$\left[\overset{+}{SCl_3}\right]\bar{Cl} \text{ and } \left[\overset{+}{S_3Cl_3}\right]\bar{Cl}, \text{ i.e. } \left[\overset{Cl^6}{\underset{Cl^6}{Cl^6}}{\!\!\diagdown\!\!}\overset{+}{S}^2\right]\bar{Cl}^8 \text{ and } \left[\overset{Cl^6=S^4}{\underset{Cl^6=S^4}{}}{\!\!\diagdown\!\!}\overset{+}{S}^2=Cl^6\right]\bar{Cl}^8$$
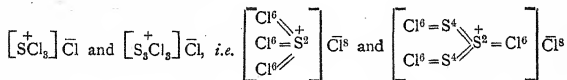
In their properties, all these halogen compounds behave as addition compounds of halogen and sulphur or selenium of the types (S, Cl_2) and (S_2, Cl_2). Intermetallic compounds (p. 856) are not formed according to the salt-valency of the elements, and these may be examples of a similar effect in non-metallic compounds. In double decompositions these compounds have the properties of their components in diminished intensity.

Sulphur oxytetrachloride, $ClSO_3.SCl_3$.—This compound is a substitution compound of SCl_4, in which one chlorine atom has been replaced by the radical of chlorsulphonic acid, $O.SO_2.Cl$. It is formed by the action of a considerable excess of damp chlorine on S_2Cl_2, and forms white needles or plates with a sharp odour, which melt at $57°$, with evolution of chlorine and sulphur dioxide. On long keeping it liquefies as a result of the decomposition:

$$ClSO_3.SCl_3 \longrightarrow SO_2Cl_2 + SOCl_2.$$
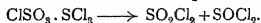
Thiocyanates of Sulphur.—Both the compounds $S(CNS)_2$ and

[1] Sugden, *Parachor and Valency*, London, 1930, p. 136 ; *cf.* Pearson and Robinson, *J. Chem. Soc.*, 1933, 1427, who consider that the parachor evidence favours II.

[2] Brockway and Pauling, *Proc. Nat. Acad. Sci.*, 1933, **19**, 68 ; Braune and Knoke, *Z. physikal. Chem.*, 1933, **21B**, 297.

[3] *J. Chem. Soc.* 1934, 485.

[4] Lowry and Jessop, *J. Chem. Soc.*, 1929, 1421 ; 1930, 782.

$S_2(CNS)_2$ may in many respects be compared with the halogen compounds, but they have somewhat different properties from the latter. $S(CNS)_2$ is formed by the action of sulphuretted hydrogen on an ethereal solution of free thiocyanogen:

$$2(CNS)_2 + H_2S \longrightarrow S(CNS)_2 + 2HCNS.$$
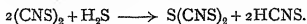
It forms snow-white crystals which soon decompose to give a yellow coloration and suddenly explode in a harmless way, emitting an orange smoke. $S_2(CNS)_2$ is formed by the action of the thiocyanates of heavy metals on S_2Cl_2 in carbon bisulphide solution:

$$Hg(CNS)_2 + S_2Cl_2 \longrightarrow S_2(CNS)_2 + HgCl_2,$$
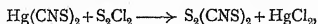
and may be frozen out in the form of white crystals which melt at $-3.5°$; these, on melting, also undergo decomposition and fulminate sooner or later after the mass has turned yellow. Water decomposes these compounds, which, however, dissolve unchanged in many organic solvent media.[1]

[1] Lecher, Wittwer and Goebel, *Ber.*, 1922, 55, 1481.

V. THE NITROGEN, PHOSPHORUS ARSENIC GROUP

In the fifth group of the periodic system (N, P, As, Sb, Bi) the resemblance of the elements to one another is less than in most of the other groups. The first and last, in particular, differ largely from the others. As, however, the most important valencies of these elements (three and five) are present in all the members of the group, their compounds are at least similar in formula and often in structure as well. In no other group, with the exception of the fourth, is the transition from the non-metallic to the more metallic elements so marked or with such an effect on the character of the compounds. Even between nitrogen and phosphorus, or between the more metallic antimony and bismuth, the chemical properties change to a very considerable extent. There is seldom any obvious relationship except between two adjacent members of the series. Among the tervalent hydrogen compounds, those of arsenic, antimony and bismuth resemble each other considerably; the similarity is less noticeable in the halogen compounds, and less still in the oxygen compounds of these three elements. Similarities between two neighbouring members are often clearly marked, e.g. in the reactions of the phosphates and arsenates; if a third member is taken into consideration the comparison breaks down almost completely.

The great variety in the properties and composition of the oxygen compounds in the lighter members of the group is characteristic, as compared with the monotonous habit of the oxides of the heavier members; again, the great stride from the explosive halogen compounds of nitrogen to the stable and quite different halides of the heavier elements is noteworthy. This is paralleled by the difference between the stable hydride of nitrogen, ammonia, with its extreme tendency to combine with other substances, and the relatively inactive and easily decomposed hydrides of the other elements. The great capacity of ammonia to combine with acids and salts, leading to the formation of ammonium salts and ammines, is weakened in phosphine, PH_3, almost to extinction. The phosphorus compound P_2H_4 corresponds to hydrazine only in formula, and not in behaviour, while the solid phosphorus hydrides find no analogues in formula or behaviour, either in nitrogen compounds or in those of the more metallic elements.

THE HYDRIDES OF THE ELEMENTS
OF THE FIFTH GROUP

Preparation of ammonia—Of phosphine, arsine and stibine—Properties—Ammonium compounds—Ammines—Free ammonium—Phosphonium compounds—Amides and imides of the metals—Amidosalts—Nitrides, phosphides, arsenides and stibides of the metals—Nitrides of P, B, Si, Ti

THE following hydrides of these elements are known :

NH_3	N_2H_4		HN_3
Ammonia.	Hydrazine.		Hydrazoic acid.
PH_3	P_2H_4	$P_{12}H_6$	P_9H_2
Gaseous,	Liquid,	Yellow,	Orange,
		solid hydrides of phosphorus.	
AsH_3	SbH_3		BiH_3
Arsine.	Stibine.		Bismuth hydride.

Solid hydrides As_2H_2, Sb_2H_2, As_4H_2 have also been described, and some evidence has been advanced for Bi_2H_2.

Ammonia is by far the most important of these compounds. Its *preparation* may be carried out either (*a*) synthetically, from its elements; or (*b*) by hydrolysis of nitrides and amides; or (*c*) by reduction of oxides of nitrogen.

The synthetic method of preparation has become of great importance. It takes place when mixtures of nitrogen and hydrogen under high pressures (*e.g.* 200 atm.), and at a temperature of about 500°, are brought in contact with suitable catalysts. The reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is reversible and exothermic. At lower temperatures the equilibrium shifts in favour of ammonia. The pressure diminishes to half its initial value when ammonia is formed, since every four molecules of gas originally present give only two molecules of ammonia. Increase in pressure favours the process by which the volume is diminished, and the formation of ammonia is therefore assisted by high pressure. According to the law of mass action, the ratio between the components on the right and left sides of the above equilibrium is as in (I.), and their partial pressures (P and p respectively) according to (II.) :

$$\text{I.} \quad \frac{[NH_3]^2}{[N_2] \cdot [H_2]^3} = K. \qquad\qquad \text{II.} \quad \frac{P_{NH_3}}{p^{\frac{1}{2}}_{H_2} \times p^{\frac{3}{2}}_{N_2}} = K_p.$$

Haber[1] determined K_p at various temperatures and pressures, and from a consideration of the heat of formation of ammonia (11·0 Cal. at o°) and its specific heat, has shown that K_p can be calculated from the formula[2]

$$\log_{10} K_p = \frac{2888}{T} - 6\cdot134 \qquad\qquad (T = \text{abs. Temp.}).$$

In a mixture of 3 vol. hydrogen and 1 vol. nitrogen the following yields are obtained :

PERCENTAGE OF AMMONIA AT VARIOUS TEMPERATURES AND PRESSURES

$t°$.	1 atm.	30 atm.	100 atm.	200 atm.
200	15·3	67·6	80·6	85·8
300	2·18	31·8	52·1	62·8
400	0·44	10·7	25·1	36·3
600	0·049	1·43	4·47	8·25
800	0·0117	0·35	1·15	2·24

According to these results the best yield of ammonia is obtained by working at the lowest possible temperature. But equilibrium is only slowly attained under such conditions; at the normal temperature no noticeable combination takes place, nor is there any decomposition of ammonia. Reaction takes place quickly at high temperatures, but the equilibrium is not favourable to the synthesis of ammonia Medium temperatures must therefore be employed, the reaction velocity increased by the addition of catalysts, and the formation of ammonia increased by pressure. In this way, at about 500°, a yield of 13 per cent. NH_3 is obtained, which may be removed from the gaseous mixture by absorption in water or liquefaction, and the unconverted gases again brought to a condition of equilibrium (Haber). If 1000 atm. pressure is used at about 600° the yield is above 40 per cent. The use of the highest pressures[3] naturally decreases the resistance of the pressure vessels to the diffusion of hydrogen; but in spite of this it has been carried out technically.

A great deal of work has been done to discover suitable catalysts and to elucidate the mechanism of their action. Metallic osmium is an excellent contact catalyst, but is not technically applicable owing to its high cost. Pumice covered with metallic sodium, metallic uranium, molybdenum, tungsten or iron may be used, and also the carbides and nitrides of these substances. It appears that pure metals are easily poisoned by sulphur, arsenic and phosphorus, this effect being least with molybdenum, which can be introduced as MoO_3 and then forms a nitride. Mixtures of metals not too closely allied in their chemical behaviour work better, and their

[1] *Z. Elektrochem.*, 1914, **20** ; 1915, **21**, 191.

[2] See also Partington and Shilling, *The Specific Heats of Gases*, London, 1924 ; Shilling, *Trans. Faraday Soc.*, 1926, vi, **22**, 396.

[3] Claude, *Compt. rend.*, 1920, **169**, 649 and 1039 ; **170**, 274.

hydrides, carbides, nitrides or cyanides can also be employed. For instance, iron, which takes up hydrogen, and molybdenum, which takes up nitrogen, form a suitable pair. The most useful catalysts, however, are those metals which are activated by a layer of oxide, such as MgO or Al_2O_3, on their surface. These coatings favour the emergence of the active points in the metal, e.g. in iron, of the more active α-iron, each atom of which can take up two hydrogen atoms. It was formerly doubted whether the iron could also take up nitrogen in the same way, but that is now beyond question (cf. p. 632) and an alkali-activated iron catalyst is commonly used commercially.

The reverse effect, the catalysis of the decomposition of ammonia, has also been studied; with tungsten, an imide, $W_n(NH)$, is first formed and later a nitride.[1] Exchange reactions with deuterium also take place in the gaseous phase, the slow reaction being $D + NH_3 \rightleftharpoons NH_2D + H$, the other steps $H + D_2 \rightleftharpoons HD + D$ and $D_2 \rightleftharpoons 2D$ being rapid.[2]

At very high temperatures the synthesis of ammonia may be carried out without the aid of catalysts. The ammonia concentration reaches a minimum at 1100° and increases again at higher temperatures. While it only amounts to 0.003 volume per cent. at 1100°, it is 1.23 volumes per cent. at 2400° (Maxted). Ammonia is synthesised in England at Billingham by the Haber process.

Ammonia is formed by the hydrolysis of amides and nitrides. The acid amides first yield ammonium salts (I.), while those of metals give ammonia immediately (II.):

I. $\begin{array}{c} CH_3CO \,|\, NH_2 \\ + HO \,|\, H \\ \hline CH_3CO_2H + NH_3 \end{array}$ II. $\begin{array}{c} Na \,|\, NH_2 \\ + HO \,|\, H \\ \hline NaOH + NH_3 \end{array}$
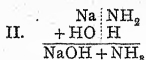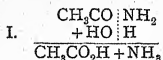
The first reaction takes place slowly, the latter very energetically. Neither is much used in the preparation of ammonia. On the other hand, ammonia may be obtained technically by hydrolysing nitrides of the metals. They are more easily hydrolysed than those of the non-metals, which are often very difficult to decompose (cf. pp. 632 and 634). Nitrides of magnesium, aluminium, calcium, beryllium and lithium in particular (which, although they are not in one group, are very close together in the periodic system) evolve ammonia copiously on being moistened with water:

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3.$$
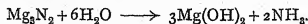
ND_3 was obtained[3] by this reaction using D_2O, the m.pt. being 199° T. (NH_3, m.pt. 195.2°) and b.pt. 242° T. (NH_3, b.pt. 239.8°).

The hydrolysis of nitrides is a very valuable property, since they are conveniently obtained, some from the metal and atmospheric nitrogen,

[1] Mittasch and Frankenburger, Z. Elektrochem., 1929, 35, 920.
[2] A. Farkas, J. Chem. Soc., 1936, 26.
[3] Taylor and Jungers, J. Amer. Chem. Soc., 1933, 55, 5057.

and others, like aluminium nitride, from the oxide, carbon and nitrogen on heating to a high temperature (Serpek). Of the nitrides of the non-metals, that of carbon, cyanogen, is useful for the production of ammonia. When, for example, cyanides are boiled with alkali, they are hydrolysed with the formation of ammonia. The hydrolysis of a more complex but very easily prepared cyanide, calcium cyanamide, $Ca=N-C\equiv N$, is used technically especially in the U.S.A.; on treatment with steam all the nitrogen is split off as ammonia:

$$CaCN_2 + 3H_2O \longrightarrow CaCO_3 + 2NH_3.$$
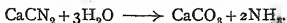
It undergoes a similar decomposition in the soil, and hence finds application as a nitrogenous fertiliser. The calcium cyanamide is prepared by the action of nitrogen on calcium carbide at about 800°, but the formation of the carbide and combination with nitrogen may be carried out in one operation by heating a mixture of lime and coke in a stream of nitrogen, preferably in the presence of a few per cent. of calcium chloride or similar salts, which accelerate the reaction.[1]

The reduction of oxides of nitrogen by hydrogen results in the formation of ammonia and can be carried out in two ways. If hydrogen previously prepared is used and the action proceeds in the gaseous state, the reduction is only completed at fairly high temperatures, though contact materials accelerate it. The oxides of iron, tin, zinc and copper act as catalysts, but metallic platinum is particularly effective, and in its presence reaction sets in at room temperature and may proceed with explosive violence. If, however, the reduction is carried out in solution and nascent hydrogen is employed, both oxides and acids of nitrogen can be reduced to ammonia. The reduction is most successful in alkaline solution, e.g. if the hydrogen is produced from zinc and caustic soda. Nitrates can be quantitatively reduced to ammonia in this way, and some alloys are specially suitable for the purpose, e.g. Devarda's alloy, which contains zinc, aluminium and copper.

The chemical mechanism of a number of technically important methods of formation of ammonia is not very clear. Among these is its formation by the dry distillation of nitrogenous substances, e.g. coal. In addition to coal gas, much ammonia is obtained, but it is only one of many products containing nitrogen (cyanides, thiocyanates, organic bases of all kinds), and it is formed in various ways, but mainly by processes of hydrolysis. If the dry distillation is carried out in the presence of strong bases (KOH, NaOH, soda-lime), the by-products containing nitrogen all split up to form ammonia, and a quantitative estimation of the nitrogen in organic substances may be based on a determination of the ammonia evolved.[2] Many substances containing nitrogen give a quantitative yield of ammonia, often from very complex reactions, if they are treated with dehydrating agents at high temperatures (conc.

[1] Caro and Frank, D.R.P., 1898, 10897; Cyanid-Ges., D.R.P., 1921, 150878.
[2] Varentrapp and Will, Ann., 1839, 39, 257.

sulphuric acid, phosphorus pentoxide), especially in the presence of a little mercury (Kjeldahl) or selenium dioxide. This process also serves for the quantitative estimation of nitrogen. Ammonia is also a product of the functions of certain organisms, and thus occurs in processes of putrefaction.

If it is desired to obtain small quantities of gaseous ammonia in the laboratory, commercial concentrated aqueous ammonia is warmed (*e.g.* by dropping from a tap-funnel on to solid sodium hydroxide), or an ammonium salt is heated with lime:

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O + 2NH_3.$$
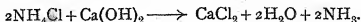
Acids cannot be used to dry the gas; nor can acid anhydrides be employed, as they yield amides, *e.g.* $SO_3 + NH_3 \longrightarrow SO_2(OH)(NH_2)$. Dehydrated salts, like calcium chloride, are also useless for the purpose, since they combine with ammonia to form ammines; calcium oxide or sodium hydroxide must therefore be used. Very dry gas is obtained if the gas is first combined with a salt, as in the compound $CaCl_2 . 8NH_3$, and the ammonia driven off by heat.

Preparation of PH₃, AsH₃, SbH₃ and BiH₃.—Only two of the methods used in the production of NH_3 are applicable without modification to the production of PH_3, AsH_3, SbH_3 and BiH_3—reduction by nascent hydrogen and hydrolysis of metallic phosphides, arsenides, stibides and bismuthides.

Reduction by nascent hydrogen is carried out in such a way that soluble compounds of phosphorus, arsenic or antimony in acid solution are acted upon by metals soluble in the acid, usually by zinc. The hydrogen compounds thus prepared generally escape with the excess of unused hydrogen, with which they are mixed in a very small proportion. Although it is not impossible to carry the reduction quantitatively to AsH_3, it is difficult to effect this owing to the action of the zinc in partially precipitating the more noble arsenic or antimony from solution. The elements thus precipitated are attacked only with difficulty or not at all, though white phosphorus in the presence of zinc and acid gives hydrogen phosphide.

The hydrolysis of metallic phosphides, arsenides, stibides and bismuthides is comparable to that of the nitrides, but proceeds more quickly, gives a better yield, and is the best method of preparation:

$$Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3,$$
$$Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3,$$
$$Na_3As + 3H_2O \longrightarrow 3NaOH + AsH_3,$$
$$Zn_3Sb_2 + 6H_2O \longrightarrow 3Zn(OH)_2 + 2SbH_3,$$
$$Mg_3Bi_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2BiH_3.$$
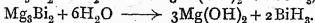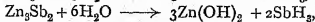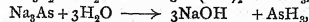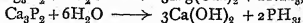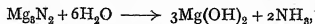
Water effects this hydrolysis in the alkali compounds. In those of the alkaline earths, and particularly of the heavy metals, it is best to assist it by acids, which dissolve the metallic hydroxide formed.

The hydrides formed on decomposition with water are practically free from hydrogen, but when acids are used they always contain it in larger or smaller quantities. The hydrogen which is formed as the main product in the hydrolysis of bismuthides contains only a few parts of BiH_3 per million.[1] The hydrides may be separated from hydrogen by freezing them out.

There are some special methods of preparing phosphine which cannot be used in the preparation of the other hydrogen compounds of this group. The hydrolysis of phosphorus is carried out in the same way as that of chlorine, which gives its hydride and an oxy-acid (p. 362). Phosphorus yields its hydrogen compound, PH_3, and the lowest of its acids, hypophosphorous acid, H_3PO_2. The reaction is completed with more difficulty in neutral solution than when the $H^{\cdot}$ ions formed are taken up by alkali; (yellow) phosphorus is therefore heated with caustic potash solution. Another method of preparation is to heat acids of medium degree of oxidation, H_3PO_2, H_3PO_3, or their salts, which decompose in a double reaction into two products, one poorer in oxygen and one richer in oxygen. Just as a chlorate yields chloride and perchlorate on heating, so a hypophosphite decomposes into a phosphate and phosphine:

$$2H_3PO_2 \longrightarrow H_3PO_4 + PH_3.$$

The phosphine obtained in all these reactions is never pure, but is always mixed with the other hydrides of phosphorus, P_2H_4, in particular. This impurity gives it the property of spontaneous inflammability in air, and it must either be removed by strong illumination or absorbed by solvents (alcohol) or condensed by cooling in a freezing mixture. PH_3 is obtained quite pure by decomposing phosphonium iodide with caustic potash or by water: $PH_4I + KOH \longrightarrow PH_3 + KI + H_2O$.

Bases liberate PH_3 from phosphonium salts even more easily than ammonia from ammonium salts, as on the one hand PH_3 is sparingly soluble in water, and on the other the tendency of phosphonium compounds to dissociate is greater than that of the ammonium compounds. On dilution of an aqueous solution, PH_4I dissociates to such an extent at room temperature that the solubility of PH_3 is exceeded and the gas is evolved.

Physical Properties.—All these hydrides are gases which condense to colourless liquids at low temperatures, and on further cooling form crystalline solids. Under atmospheric pressure their boiling and melting points are:

	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Boiling point .	$-33 \cdot 5°$	$-86 \cdot 2°$	$-55°$	$-18°$	?
Melting point .	$-78°$	$-132 \cdot 5°$	$-119°$	$-88°$	?

While the boiling and melting points of the hydrides rise with

[1] Paneth and Winternitz, *Ber.*, 1918, **51**, 1728.

increasing molecular weight from phosphorus to antimony, the boiling and melting points of ammonia are unexpectedly high, owing to the association of NH$_3$ molecules in the condensed state, which is similar to that of the H$_2$O molecules (*cf.* p. 399). In the gaseous state, ammonia, like water, is unimolecular; its depolymerisation on evaporation similarly requires a considerable amount of heat from the surroundings, so that the evaporation of ammonia "generates cold," and is used in the refrigerating industry. From the physical standpoint ammonia and water have much in common in other ways. The specific conductivity of ammonia (ca. 1×10^{-8} recip. ohms) is of the same order of magnitude as that of water, its dielectric constant (ca. 22), although markedly smaller than that of water, is still fairly high. It is probably on account of this that liquid ammonia is a very good ionising medium for inorganic salts, being the best after water and liquid hydrocyanic acid. It dissolves more salts and in greater quantities (*cf.* below) than any other liquid except water (*cf.* p. 400). Further, it shows a remarkable tendency to occupy supplementary valency positions with formation of numerous ammines analogous to the hydrates given by water. These properties disappear in PH$_3$, AsH$_3$ and SbH$_3$; nor are these hydrides polymerised in the liquid condition; they are not good solvents for salts, and do not form many addition compounds.

Ammonia, like all easily condensed gases, is very strongly adsorbed by porous materials. The adsorption of a gas, indeed, is almost parallel to its condensibility. Thus coconut charcoal at 0° under atmospheric pressure adsorbs 170 times its volume of ammonia, but only 69 times its volume of phosphine. The high solubility of ammonia in water is partly due to its resemblance to this solvent—they combine with polymerisation to (H$_2$O)$_m$(NH$_3$)$_n$. The ammonia pressure above the solution is less than would be expected from Henry's Law, so that it is not a case of simple solution. The solubility is also affected, but to a lesser extent, by the chemical addition of water, which leads to the formation of NH$_4$OH, possibly a resonance variety related to H$_3$N—H—OH (*cf.* p. 347), and of NH$_4$· ions. While PH$_3$, AsH$_3$ and SbH$_3$ all dissolve at room temperature only in five times their volume of water, *i.e.* in very many times their weight of water, the solubility of ammonia under atmospheric pressure in 1 g. water is :

Temp. . .	−30°	0°	10°	30°	50°	80°	100°
g. NH$_3$ . .	2·781	0·875	0·679	0·403	0·229	0·154	0·074

Ammonia dissolves less easily in organic solvents than in water, while the other substances of this group dissolve more readily in them ; thus alcohol takes up about 75 times as much SbH$_3$ as water does, and one volume of carbon disulphide dissolves 250 volumes of this gas.

The high ammonia content of the concentrated aqueous solution

affects its physical behaviour. Liquefied ammonia has the very small density $d_{16\cdot5^\circ} = 0\cdot613$, and hence solutions of the gas are also lighter than water. A concentrated solution at room temperature contains almost a third of its weight of NH_3. The following table shows the density of some solutions of ammonia:

Per cent. NH_3 .	34·9	28·3	21·7	15·6	9·9
d_{15° . . .	0·88	0·90	0·92	0·94	0·96

An odour which is very difficult to define is common to all the gases of this group; that of ammonia is most pungent. Whilst ammonia gives rise to no special poisonous symptoms if breathed in small quantities, or even in considerable amounts, the other gases are exceedingly dangerous. Antimony hydride can bring about the death of mice at a dilution of 1/100th per cent.

Spontaneous Decomposition. — The stability of these gases is indicated by their heat of formation, which is strongly positive for NH_3 and PH_3, and strongly negative for AsH_3 and SbH_3:

	NH_3	PH_3	AsH_3	SbH_3
Heat of formation .	+ 11·2	+ 11·6	− 36·7	− 81·8 Cal.

AsH_3 and SbH_3 therefore decompose spontaneously[1] even at room temperature, and as the metals formed are not acted upon by the hydrogen, the decomposition is finally quantitative. The ammonia equilibrium has been discussed on p. 606. NH_3 is decomposed photochemically only if exposed to radiation of wave-length 2100 Å, the mechanism postulated being $NH_3 \rightleftharpoons NH_2 + H$; this view is supported by the fact that NH_2D is produced ($NH_2 + D \rightleftharpoons NH_2D$) if atomic deuterium (formed by exposing D_2 to radiation of wave-length 2537Å) is introduced.[2] The decomposition of AsH_3 and SbH_3 always takes place slowly (even bismuth hydride is not very unstable when once formed), and more rapid decomposition only sets in if the velocity of reaction is increased by raising the temperature. One consequence of the strongly endothermic nature of AsH_3 and SbH_3 is that by suitable arrangements these gases may be made to explode. With AsH_3 this can be done by detonation with mercury fulminate, but with SbH_3 it is sufficient to warm it to 200° or to heat locally, when not only does the gas decompose explosively with the appearance of a red flame, but even the liquid or highly cooled gas is decomposed, even if 40 per cent. hydrogen is present as impurity.

The thermal decomposition of the hydrogen compounds of arsenic, antimony and bismuth is an exceptionally sensitive test for these three elements, known in analysis as Marsh's test. The decomposition of arsenic hydride gives a shining, blackish mirror, which is

[1] See Stock and co-workers, *Ber.*, 1904, **37**, 885 ; 1907, 40, 532.

[2] Taylor and Jungers, *J. Chem. Physics*, 1934, **2**, 452.

easily soluble in hypochlorite, while that of antimony and bismuth
hydrides leaves a more brownish mirror, insoluble in hypochlorite.
The mirror formed by bismuth can be distinguished from both the
others, as its colour deepens on treatment with ammonium polysulphide,
while those of arsenic and antimony are weakened almost to the
vanishing point.

Reducing Action.—These gases easily give up hydrogen, and thus
behave as reducing agents. Whilst ammonia shows this property only
at higher temperatures, the other hydrides reduce in the cold, especially
in the presence of moisture. Thus antimony hydride is very susceptible
to moist oxygen, and PH_3, AsH_3 and SbH_3 in aqueous solution behave
as strong reducing agents, in that they not only reduce the usual
oxidising agents, permanganate, chromate and even sulphuric and
sulphurous acids, but also decompose solutions of salts of heavy metals,
especially the more noble ones, depositing the metal. The reduction
of silver nitrate is most characteristic and proceeds in two steps with
all three gases; if they are passed into the concentrated solution an
intense yellow deposit is first formed, the chemical composition of
which has not been ascertained with certainty. On further reduction,
or on keeping, it decomposes with the separation of black metallic silver,
so that the final reaction with arsine occurs according to the equation

$$2AsH_3 + 12AgNO_3 + 3H_2O \longrightarrow As_2O_3 + 12Ag + 12HNO_3.$$
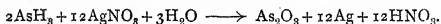
As the yellow precipitate as well as the black silver can be seen very
well at great dilutions, this is a good method of proving the presence
of these gases (Gutzeit's test): in this, a filter paper cap which is either
saturated with concentrated silver nitrate solution or on which a crystal
of the nitrate is laid, is placed over the exit from the vessel in which
the gas is evolved. Mercury salts, etc., are also reduced to the metal by
the gases, but copper chloride first absorbs them, with some formation
of a double compound. It may be that arsenides, e.g. $Ag_3As . 3AgNO_3$,
and phosphides are always formed as intermediate products; the latter
especially seem to be mixed with the final products.

All the gases of this group, including ammonia, are combustible,
the colour of the ammonia flame being yellow, that of phosphine green,
and of arsine pale blue. The products of combustion, in addition to
water, are the acidic oxides of the elements, the degree of oxidation
depending on the quantity of oxygen present. In arsine and stibine
decomposition sets in before combustion, for if a cold object is held in
the flame it becomes covered with a film of free arsenic or antimony,
just as a coal-gas flame deposits soot on contact with cold, solid bodies.
If, on the other hand, the arsine flame is allowed to burn freely, it emits
white fumes of arsenic trioxide. In ammonia the combustion may be
carried out without the appearance of flame; if a glowing platinum
spiral is suspended in a vessel with a wide mouth, at the bottom of

which there is some warm concentrated ammonia solution, it continues to glow. The ammonia gas mixes with the air streaming in from above, and decomposition takes place so rapidly on the surface of the platinum, owing to contact action, that the temperature of the platinum is not lowered.

When ammonia gas is split up into nitrogen and hydrogen at higher temperatures, it is then even a better reducing agent than free hydrogen, as the hydrogen is set free from the ammonia in the atomic condition (nascent). All the reducing actions of hydrogen at red heat can be more readily carried out with ammonia; it reacts differently only when the nitrogen formed takes part in the reaction. For this reason the action of ammonia on some metallic oxides yields nitrides instead of the free metals.

Substitution.—The substitution of the hydrogen atoms by other elements or groups is important in ammonia, but not in the other gases. The phosphides, arsenides and stibides may certainly be looked upon as derivatives of these gases in which the hydrogen is replaced by metal, and these gases are formed by hydrolysis of the metal substitution products. But arsenides are never prepared from arsine. In ammonia one or more hydrogen atoms may be replaced by other elements. Thus by dissolving alkali metals in liquid ammonia the metal amides (I.) are obtained (*cf.* p. 625), and by decomposition with chlorine, chloramine (II.) is formed (*cf.* p. 742) :

I. $2NH_3 + 2Na \longrightarrow 2NaNH_2 + H_2$.   II. $NH_3 + Cl_2 \longrightarrow NH_2Cl + HCl$.
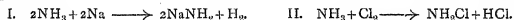
Ammonium Compounds—*Constitution and Stability.*—The chemistry of ammonia acquires quite a special importance from the large number of solid supplementary valency compounds with all kinds of positive elements. The secondary valency compounds with the hydrogen of acids are the most important, and are known as ammonium compounds :

$[H]Cl + NH_3 \longrightarrow [H(NH_3)]Cl$ $[H]_2SO_4 + 2NH_3 \longrightarrow [H(NH_3)]_2SO_4$.
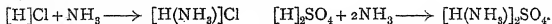
The addition of the electrically neutral substance, ammonia, does not alter the valency of the central atom (*cf.* p. 282); the hydrogen atom remains univalent as before, and thus the whole ammonium radical is also univalent.

It may be supposed that as soon as it is once formed this radical, $[H(NH_3)]'$, is arranged in such a way that all four hydrogen atoms play the same part with respect to the nitrogen atom, so that it may acquire the following formulation :

$$\left[\begin{array}{c} H \\ H : \overset{..}{\underset{..}{N}} : H \\ H \end{array} \right]^{.}$$
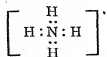
This may result from the following electronic rearrangement (see also p. 347) :

$$H = \overset{H}{\underset{H}{N^2}} + H = Cl^6 \longrightarrow \left[H = \overset{H}{\underset{H}{N}} = H \right] \overline{Cl}^8.$$
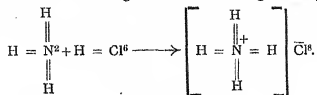
If in some reactions only one of the hydrogen atoms is required, the remainder can immediately rearrange themselves in the form $[H(NH_3)]$ as ammonia. This happens when hydroxyl ions are added, which neutralise the acidic hydrogen atom functioning as the central atom according to the formulation $[H(NH_3)]$, so that ammonia is liberated.

The power of combining in this way with the hydrogen of acids is not limited to one ammonia molecule, but several may be taken up, according to the nature of the acid radical. Just as the metallic halides yield more stable ammonia addition products than all other metallic salts, so the halogen hydracids give the most stable ammines. Of the polyammines of the hydrogen compounds, the following are known:

$$[H(NH_3)_4]Cl \quad \begin{array}{l} [H(NH_3)_2]Br \\ [H(NH_3)_4]Br \\ [H(NH_3)_7]Cl \end{array} \quad \begin{array}{l} [H(NH_3)_2]I \\ [H(NH_3)_4]I \\ [H(NH_3)_7]Br \end{array} \quad \begin{array}{l} [H(NH_3)_4]NO_3 \\ [H(NH_3)_7]I \end{array}$$
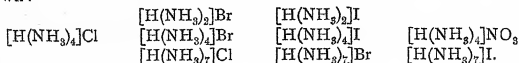
These compounds are stable only at low temperatures, and are formed from the simple ammonium salts $[H(NH_3)]R$ and anhydrous ammonia. Some can be kept above 0°. On warming they decompose in stages, and finally leave behind compounds with only one molecule of ammonia:

$$[H(NH_3)]Cl \qquad [H(NH_3)]Br \qquad [H(NH_3)]I \qquad [H(NH_3)]NO_3.$$

Their last ammonia molecule is removed by further heating; indeed some are so unstable that they cannot retain the ammonia even at room temperature, e.g. the compounds of the weaker acids, such as boric and silicic acids, and especially that derived from water. The pure hydroxide, $[H(NH_3)]OH$, is extensively decomposed at room temperature, the equilibrium of the reaction $[H]OH + NH_3 \rightleftharpoons [H(NH_3)]OH$ being very much to the left (cf. p. 620). Other "ammonium salts" are indeed still stable at room temperature, but decompose at a slightly higher temperature. Thus the addition product with hydrogen peroxide, $[H(NH_3)]O.OH$, is formed as water-clear crystals which melt at 14° by passing NH_3 into an ethereal solution of H_2O_2; at a still lower temperature ($-10°$) the diammine $[H(NH_3)]O.O[(NH_3)H]$ decomposes. This compound [1] may be considered to be "ammonium peroxide" $(NH_4)_2O_2$.

The ammines (ammonium salts) of carbonic acid, of hydrogen sulphide and other acids of medium strength decompose at moderate temperatures (cf. p. 619). Some ammonium salts are capable of existing at higher temperatures, for example those of the halogen acids, nitric acid, sulphuric acid, and indeed of most strong acids; however, they all decompose when a certain temperature is reached. The decomposition is reversible, $[H(NH_3)]Cl \rightleftharpoons HCl + (NH_3)$, and a definite pressure of ammonia corresponds to each temperature. The

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[1] d'Ans and Wedig, Ber., 1913, 46, 3075.

ammonium salts are stable below a definite temperature and above a definite pressure, *i.e.* where their ammonia pressure is less than the pressure exerted above the substance. Above this temperature ammonia volatilises, and if the remaining acid is also volatile at this temperature it vaporises as well, and thus the whole substance sublimes without leaving a residue. If the mixed vapours of ammonia and the acid become cooled to a temperature which does not correspond to an ammonia pressure of above one atmosphere, they recombine; the substance only apparently sublimes, but actually it has passed through the double chemical process of decomposition and combination. If the acid is not volatile (*e.g.* phosphoric acid), the ammonia alone escapes, and the acid remains behind; recombination cannot occur in the gas phase.

It is interesting to notice that the sequence of the decomposition temperatures of the metallic salt ammines is the same as that of the hydrogen ammines, *i.e.* the ammonium salts. This is a further proof that ammonium salts are addition compounds. In the following table the decomposition temperatures of some ammonium salts are set out in parallel with those of some nickel hexammine salts. The order is the same. The phosphonium compounds of corresponding constitution are also included.

Nickel Compound.	Decomp. temp. at 760 mm.	Ammonium Compound.	Decomp. temp. at 760 mm.	Phospho- nium Compound.	Decomp. temp. at 760 mm.
$[Ni(NH_3)_6]I_2$	235°	NH_4I	400°	PH_4I	61°
$[Ni(NH_3)_6]Br_2$	209°	NH_4Br	388°	PH_4Br	39°
$[Ni(NH_3)_6]Cl_2$	176·5°	NH_4Cl	332°	PH_4Cl	– 28°
$[Ni(NH_3)_6]SO_4$	143·5°	$(NH_4)_2SO_4$	300°	...	...
$[Ni(NH_3)_6](H_2PO_4)_2$	95°	$NH_4H_2PO_4$	240°	...	...
Sulphite, Carbonate, Sulphide, Cyanide, Oxalate, Hydroxide	not obtainable at room temp.	Corres. comps.	160°	...	...
		...	...	...	...

The stability of these compounds is thus affected by the anion, as well as by the cation in which the ammonia is present. The nature of the complex [$H(NH_3)$] (and all similar ones) is not the same in all compounds, but is changeable according to the negative portion, with which the compound is bound to the molecule. This has to be emphasised, as the differences cannot be expressed by an alteration in the formulation, though they are doubtless brought about by the constitutive influence of the positions of the individual elements on each other, etc. The grouping [$H(NH_3)$] is not a fixed one; the fields of force between the atoms and their positions with respect to one another are not rigid, but may be distorted, displaced, and in one compound so closely packed that they cannot be separated from one another without difficulty, and in another so strained that the compound is easily ruptured. The constitution and properties of these and similar complexes vary and are influenced by the negative radicals associated with them. The fluctuations in properties occur within two limits in a continuous series of constitution.

The following parallel between the electro-affinity of the positive central atom and the affinity for the negative residue is frequently noticed. Weak positive radicals, if they are combined with strong negative ones, seek to strengthen their affinity. This occurs when they unite to form complexes with neutral groups, since

the complexes always show stronger electro-affinity than the bare central atoms. This is clear from the electrolysis of complex substances in which the complex radicals never appear at the electrodes as products of electrolysis, but only the nuclei, which are always present in solution as well as the complex, though often only in small quantities. In electrolysis, according to the laws of the electromotive series, those components are liberated for which the least E.M.F. is necessary, *i.e.* those which have the smallest affinity for the electric charge. If this portion is deposited, it is formed again from the unbroken complex molecules to maintain the equilibrium in the solution ; the complex radicals are thus gradually used up, though only the nuclear portion separates out. Thus the nucleus is weaker electrically, and has less affinity for electric charges. Since it attempts to strengthen this affinity to that of the ion with which it is combined by forming complexes, weak positive metals, especially if they are joined to a strong acid, show a considerable tendency to form complex compounds. On the other hand, if the same metal is united to a different acid residue, it holds the neutral group with which it is combined to form a complex compound more strongly the more electronegative the acid.[1] This rule proves to be correct in many cases, and also explains why the ammonium salts of strong acids decompose with most difficulty. A second factor which has a preponderating influence on the stability of the complex is the material and spatial suitability of the anion and cation to each other. There is a tendency to equalise the size of the anion and cation by adding on neutral groups,[2] and a connection between both phenomena is shown by the fact that the cations of smallest volume have the greatest tendency to form complexes, and are mostly in a low position in the electromotive series.

It is thus clear that the ammonium salts of various acids must possess varying stability according to the nature of the acid. In the less stable ones the ammine structure is externally apparent in so far as these smell of ammonia in the solid state and at room temperature. Even if the ammonia pressure does not reach that of the atmosphere, the free ammonia formed on placing the salt in the open air diffuses away, and if the acid is also volatile the ammonium salt gradually vanishes. Ammonium carbonate, for instance, disappears without leaving a residue on exposure in the air. But there are also salts of strong acids in which the ammonia is very firmly combined and which do not smell of it very much. At a slightly higher temperature they often undergo considerable loss. In $NH_4Cl \rightleftharpoons NH_3 + HCl$ the equilibrium lies well to the left, so that the products of dissociation must be present in very small quantities, but if an attempt is made to remove them the salt is gradually decomposed. Ammonium chloride therefore loses weight noticeably at $100°$, and on boiling aqueous solutions they at once become markedly acid. An estimation of the remaining acid content gives at least the relative order of stability of the ammonium salts. The evolution of ammonia on boiling the solution was formerly considered to be due to hydrolysis : $NH_4Cl + H_2O \longrightarrow NH_4OH + HCl$, and it was thought that the degree of hydrolysis could be evaluated in this way, the quantity of ammonia formed

[1] Abegg and Bodländer, *Z. anorg. Chem.*, 1899, **20**, 471.
[2] Ephraim, *Ber.*, 1918, **51**, 644 ; 1920, **53**, 546.

being equivalent to the quantity of ammonia driven off. In certain solutions of the

Chloride	Nitrate	Sulphate	Oxalate	Acetate
0·062	0·072	1·1	6·7	7·0 per cent.

of the whole amount of salt was hydrolysed. The process is, however, better considered not as hydrolysis but as the natural splitting off of ammonia according to the equilibrium $[H(NH_3)]R \rightleftharpoons HR + NH_3$. The loss of ammonia on boiling solutions of ammonium chloride is to be borne in mind in the quantitative estimation of ammonia. It is avoided by adding acids with compact anions, such as H_2PtCl_6, to which the ammonia is more firmly linked than to the hydrogen atom of hydrochloric acid.

The more H ions are present the more the equilibrium $[H(NH_3)]R \rightleftharpoons H^+ + NH_3 + R'$ is moved to the left. Excess acid therefore favours the formation of ammonium salts, and the acid ammonium salts, e.g. $(NH_4)HS$ or $(NH_4)HCO_3$, are more stable than the corresponding normal ones; $(NH_4)_2S$ can only be obtained at $-18°$ by mixing ammonia and hydrogen sulphide gases, but the white crystals formed immediately lose ammonia on warming, and are transformed to $(NH_4)HS$. This salt, which also consists of colourless crystals, decomposes quickly in open vessels into the two gases, but gives a pressure of only one atmosphere at $32·5°$. Aqueous solutions of such salts smell of ammonia and sulphuretted hydrogen even at room temperature, for the dry salt at $10°$ already has a dissociation pressure of 184 mm., and at $25°$, of 500 mm. mercury. When the aqueous solution is diluted, the $(NH_4)HS$ exerts only a portion of its whole pressure, so that it is still more decomposed than the solid salt. With reference to ammonium sulphide, compare also p. 527.

Similar effects are observed in ammonium carbonate, only here the salts are somewhat more stable (cf. p. 810). Solid $(NH_4)_2CO_3$ decomposes very easily, giving off ammonia to form $(NH_4)HCO_3$; this salt is much more stable if absolutely dry, when its dissociation pressure at room temperature is less than 1 mm. of mercury. This phenomenon of retarded dissociation is found in other ammonium salts. Ammonium chloride can be gasified if it is very dry without undergoing the volume increase corresponding to decomposition into $HCl + NH_3$, or at least the action is considerably delayed. Similarly, NH_3 and HCl may be brought together in the absolutely dry condition without combination taking place. This phenomenon recalls the observation that the union of oxygen and hydrogen if dry can no longer take place with explosion, that sodium does not burn in absolutely dry oxygen, etc., and is a further example of the importance of the presence of traces of water for the progress of chemical reactions (Baker).

If the union of carbon dioxide and ammonia is carried out in the

absence of water, no ammonium carbonate can be formed. First an ammonia molecule is added on to a carbon dioxide molecule with the formation of an amido-acid, carbamic acid :

$$C\!\!\begin{array}{c}\diagup O\\ \diagdown O\end{array} + \begin{array}{c}NH_2\\ H\end{array} \longrightarrow C\!\!\begin{array}{c}\diagup NH_2\\ =O\\ \diagdown OH\end{array} .$$
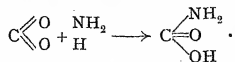
In a similar way, NH_3 combines with sulphur trioxide with the formation of amidosulphonic acid, or with phosphorus pentoxide, to give amidophosphoric acids (*cf.* p. 649).

Of the ammonium compounds, ammonium hydroxide, NH_4OH, *i.e.* $[H(NH_3)]$. OH, is of special interest. As water is only a very weak acid, its ammonia addition product is very unstable, and in aqueous solution is very much split up into its components. It nevertheless exists in small quantities in solution, as shown by the alkaline reaction of aqueous ammonia. The dissociation of the hydrogen atom in H.OH is strengthened (*cf.* p. 617) by the addition of ammonia and a greater number of OH′ ions is also obtained than in pure water. The actual quantity is always very small, as can be seen from the low conductivity of aqueous ammonia, its small influence on the velocity of saponification of esters, and the insensitiveness of many indicators towards this base. The quantity of NH_4OH molecules present as such in solution has not been accurately found, but it must be very small to give the above results. There is evidence also for the following equilibrium : $NH_3 + H_2O \rightleftharpoons H_3N - H - OH \rightleftharpoons NH_4^{\cdot} + OH′$ (see p. 347). The salts of ammonium hydroxide, *i.e.* the ammines of stronger acids, are, however, good conductors in solution, and as they do not give off any appreciable amount of NH_3 they are neutral in reaction. These salts are similar to those of the heavier alkali metals as far as crystalline form and solubility are concerned (pp. 239, 242). These properties are due to the NH_4 radical having a similar volume to these metals—almost the same as that of rubidium. Thus the well-known potassium precipitation reactions, *e.g.* those with H_2PtCl_6, with $Na_3[Co(NO_2)_6]$, with tartaric acid, etc., are given by ammonium salts in a very similar way, the solubility of these salts being often, but not always, between that of the potassium and rubidium compounds. The detailed properties of ammonium salts are dealt with in the consideration of their respective acids.

Ammines (Ammoniates).—The metals of small atomic volume (*cf.* the curve, p. 32) have a special tendency to add on ammonia, and can generally take up a maximum of three molecules of gas per main valency, *e.g.* the compounds

$$[Ag(NH_3)_2]Cl \qquad [Ni(NH_3)_6]Cl_2 \qquad [Al(NH_3)_9]Cl_3$$
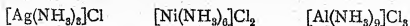
are known.

The alkaline earths and lithium are able to add on four ammonia molecules per main valency :

$$[Li(NH_3)_4]Cl \qquad [Ca(NH_3)_8]Cl_2,$$

but this maximum type is not always attained and its occurrence depends on the nature of the acid radical. Phosphates, carbonates, sulphides, etc., never give the maximum type, and of the hydroxides, only that of nickel—a metal of very small volume—gives the compound with six ammonia molecules. If the acid radical is very large, *e.g.* if it is made up of aromatic organic nuclei or of complex inorganic acids as in $\left[Co \begin{matrix} (NO_2)_4 \\ (NH_3)_2 \end{matrix} \right]'$, octammines of bivalent metals are formed (p. 301). These compounds can be produced by the action of gaseous ammonia on the dehydrated salts, and from some they are also precipitated from aqueous solution on the addition of ammonia ; they lose the ammonia again on warming, though the last portion of it often goes off with simultaneous decomposition of the salt, just as many hydrates cannot lose their water without decomposition. The ammines of tervalent cobalt, chromium, platinum, etc., are of special interest and have already been fully discussed on pp. 310, 333. These are exceptionally stable and cannot be deprived of their ammonia by dry heating without further decomposition.

It is remarkable that on addition of ammonia to solutions of some salts the metal hydroxide is precipitated, while with others, especially with bivalent metals, the formation of an ammine causes the hydroxide to remain dissolved (Zn, Ni, Cu, Cd, Ag ; and in conc. ammonia Mn, Co, Cr). The fact that water is a stronger dipole than ammonia would suggest that ammines would not be stable in presence of water ; but the stability of these ammines is not dependent only on the permanent dipoles present but also on the induced dipoles due to the polarising action of a strong dipole on a weak one. As the ammonia molecule is greater in volume than the water molecule, the induction effect is greater, and so the sum of the permanent and induced dipolarity is greater for ammonia than for water, provided the ion is active in induction. This applies to those ions which form soluble hydroxides with ammonia.

Halides of non-metals also combine with ammonia, *e.g.* such compounds are known as $PCl_3 . 5NH_3$, $PCl_3 . 8NH_3$, $AsF_3 . 3NH_3$, $SbCl_5 . 6NH_3$, etc.

When substances very rich in ammonia are treated with excess ammonia, it may cling to them in such a way that at low temperatures it appears to alloy with the surface, so that considerable quantities of it are taken up. This happens in the octammines which have already been mentioned, as well as in the ammines of the salts of quadrivalent elements ($ThCl_4$, $ZrCl_4$, SnI_4), which fix great quantities of ammonia at low temperatures. In this way a kind of solid solution of ammonia

in the ammine is formed, which becomes liquid when the ammonia content is sufficient, and all kinds of mixtures of the ammine with liquid ammonia can be obtained. These liquid solutions of salt ammines may be obtained in anhydrous ammonia even at the ordinary temperature; the best known is "Divers's liquid," which is formed when ammonia gas is passed into solid ammonium nitrate. The salt gradually becomes completely liquefied; at about 28° it takes up 1 mol. ammonia, at about 0°, 2 mols., and at lower temperatures even more. The ammonia can be driven off again by warming the liquid, and Divers's liquid is a good absorbent for quantities of dry ammonia gas. No definite ammines are formed, as may be proved by examining the solidification diagrams, though a compound $NH_4NO_3 . 3NH_3$ appears at −40°. Divers's liquid is a eutectic of the two components which is liquid at room temperature. Such high-boiling solutions in liquid ammonia always appear when the dissolved substance itself contains a large amount of nitrogen—ammonium salts and ammines, but the thiocyanates and cyanides also frequently show this property. Potassium cyanide, ammonium thiocyanate, some octammines, etc., liquefy when ammonia is passed over them either at room temperature or at a slightly lower temperature. At low temperatures, however, liquid ammonia is an excellent solvent for several kinds of salts (though not as good as water), when ammine formation must usually be assumed. Salts containing nitrogen again show the greatest solubility —nitrates, nitrites, cyanides, thiocyanates, cyanates : halogen salts are also soluble with the exception of fluorides and the alkali salts. Sulphates are only slightly soluble.[1] Elements also dissolve in liquid ammonia—both non-metals (sulphur, selenium, phosphorus, iodine) and metals (alkali and alkaline earth). The non-metals dissolve initially unchanged to give colloidal solutions, but soon react with the ammonia. Thus with iodine, ammines of nitrogen iodide are formed, e.g. $NI_3 . 2NH_3$. Sulphur dissolves in liquid ammonia to give a typical purple-red to bluish-violet colloidal solution, in which the reversible process,

$$10S + 4NH_3 \rightleftharpoons 6H_2S + N_4S_4,$$

takes place. In fact, by passing sulphuretted hydrogen into a solution of nitrogen sulphide in liquid ammonia, the same blue solution is made.[2] The brown solution of phosphorus in ammonia does not contain the unchanged element; a black substance is obtained from it which is possibly an ammonia compound of a hydride of phosphorus.[3] On the other hand, the alkali metals dissolve unchanged in liquid ammonia on being cooled sufficiently, and hydrogen is evolved only at higher temperatures, when an amide of the metal is formed, e.g. $NaNH_2$.

[1] Franklin and Kraus, *Amer. Chem. J.*, 1898, 20, 820.
[2] Ruff and Geisel, *Ber.*, 1905, 38, 2659.
[3] Schenck, *Ber.*, 1903, 36, 4206.

These solutions are colloidal and of a characteristic deep blue colour. On carefully evaporating the ammonia, the metal remains behind unchanged, and separates in copper- or brass-coloured lumps; the colour is due to the state of division and is changed later on to that of the ordinary metal. It was thought for a long time that metal ammines such as $Na(NH_3)$ were present in these solutions, but on gradually removing the ammonia the pressure shows such a continuous decrease that a definite constant pressure corresponding to a compound cannot be observed. Actually, semi-solid deep blue lumps of alkali metal can be isolated merely by pressure or by centrifuging,[1] but the nature of these solutions is not yet cleared up. In the alkaline earth metals it is certain that true addition compounds are formed, since the compounds of the formula $M(NH_3)_6$ show well-defined dissociation temperatures.[2] By the action of ammonia gas at low temperatures, barium is coloured a fire-red, and calcium brown; these substances are solids and have the composition $Ba(NH_3)_6$ and $Ca(NH_3)_6$ respectively. Deep blue liquids are formed by these metals only in the presence of large quantities of ammonia, and in the calcium ammine a definite jump in the tension of the ammonia has been confirmed[3] at the point where the composition $Ca(NH_3)_6$ is passed. They are converted by CO to carbonyls $M(CO)_2$, which are solid and non-volatile and are probably polar $M^{++}(CO)_2^{--}$. Their properties are similar to those of the alkali metal carbonyls (see p. 791). Magnesium also forms an ammine of formula $Mg(NH_3)_6$ (crystals with a metallic lustre) when its amalgam is treated with ammonia.

Free Ammonium.—The problem of the preparation of free ammonium, NH_4, has not lacked investigation. The attempts have all been unsuccessful, and from the conception of the ammonium radical which is evolved above this is not to be wondered at. It would be possible to isolate $[H(NH_3)]$ if atomic hydrogen were obtainable; but this is least stable at the low temperatures which are applied in the preparation of NH_4. The existence of $[H(NH_3)]$ at high temperatures might be expected if the components were not liable to dissociation. Electrolysis of ammonium compounds which should yield free NH_4 at the negative pole by the discharge of the ions (NH_4), gives instead its decomposition products, ammonia and hydrogen. One phenomenon must be considered which perhaps stands in some relationship to the existence of free ammonium—the formation of ammonium amalgam. If sodium amalgam is added to ammonium chloride solution, or if solutions of ammonium salts are electrolysed with a mercury cathode, a semi-solid, somewhat spongy mass is obtained which has a metallic lustre and swells up on keeping. It then evolves ammonia and hydrogen continuously and finally leaves pure mercury behind. It is remarkable evidence of a content of "metallic ammonium" that, at low temperatures this amalgam precipitates metals which precede hydrogen in the electromotive series, from solutions of their salts.[4] This does not altogether prove the existence of

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[1] Ruff and Geisel, *Ber.*, 1906, 39, 828.
[2] Biltz, *Z. Elektrochem.*, 1920, 26, 374.
[3] Kraus, *J. Amer. Chem. Soc.*, 1908, 30, 653.
[4] Coehn, *Z. anorg. Chem.*, 1900, 25, 430.

ammonium in the alloy, since there may be a compound of hydrogen and mercury in it[1] which is less noble than hydrogen itself. According to Moissan's view an ammine of a hydride of mercury $[H(NH_3)]_mHg_n$ may be present in the amalgam. NH_4 also seems capable of existing in liquid ammonia at low temperatures. According to Schlubach and Ballauf,[2] the blue solution of metallic sodium in liquid ammonia is decolorised when added to a solution of ammonium iodide in liquid ammonia if the temperature is kept at $-70°$. In that way the decomposition $NH_4I + Na \longrightarrow NH_4 + NaI$ takes place. Only a very small portion of the NH_4 formed decomposes, but when the liquid is warmed to $-40°$ decomposition sets in: $NH_4 \longrightarrow NH_3 + H$. The liquid containing NH_4 combines with elementary iodine, giving an ammonium salt: $NH_4 + I \longrightarrow NH_4I$.

Phosphonium Compounds.

Phosphine, PH_3, enters into compounds as a neutral component to a much lesser extent than ammonia. It forms addition compounds with a few metallic salts, e.g. with CuCl and the halides of aluminium and of quadrivalent tin and titanium; in this respect it resembles H_2S. Its tendency to become attached to hydrogen as a neutral component, and thus to form the phosphonium salts PH_4X, corresponding to the ammonium salts, is also only slight. Apart from its salts with the halogen hydrides, only that with sulphuric acid is known, and even that decomposes below $0°$. The phosphonium salts are formed in the same way as the ammonium salts—by union of the acids with PH_3 at temperatures below those given on p. 617 as their decomposition temperatures. They can be sublimed like ammonium salts, and resemble them in crystalline form. They are strong reducing agents, since the phosphine is easily split off; the iodide especially is so used, as the reducing action is supplemented by that of the hydrogen iodide. The large cubes of phosphonium iodide have a diamond-like lustre, and are best obtained by heating a mixture of equal quantities of iodine and phosphorus with a little water. On hydrolysing the phosphorus iodide, H_3PO_2 is probably formed as well as hydrogen iodide. The former immediately decomposes into H_3PO_4 and PH_3, and thus by the same reaction both the necessary gaseous products are formed, PH_3 and HI, which combine in the cooler parts of the apparatus. Phosphonium iodide is also formed on heating yellow phosphorus with hydriodic acid. The bromide can be prepared by the combination of gaseous hydrogen bromide and phosphine, and is also precipitated by passing PH_3 into very concentrated, cold, aqueous hydrobromic acid. The chloride is very easily decomposed, and is only formed at atmospheric pressure and very low temperature from the gases themselves.

Arsenic and antimony hydrides do not form such compounds in the ordinary way. If, however, their hydrogen atoms are replaced, especially by organic radicals, they can then form addition products. Thus tetramethylarsonium iodide, $As(CH_3)_4I$, corresponds to an ammonium salt.

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[1] Moissan, Compt. rend., 1901, 133, 715.   [2] Ber., 1921, 54, 2825.

Amides, Imides and Nitrides of the Metals.

Just as the hydrogen atoms of water can be replaced by metals, so derivatives of ammonia are known in which one or more of the hydrogen atoms are replaced:

$$HOH \longrightarrow NaOH \qquad\qquad H_2O \longrightarrow MgO$$
$$HNH_2 \longrightarrow NaNH_2 \qquad H_2NH \longrightarrow PbNH \qquad H_3N \longrightarrow Mg_3N_2.$$
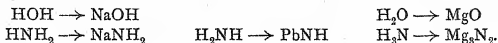
The substitution products are called

$$-NH_2 \qquad\qquad =NH \qquad\qquad \equiv N$$
Amides.   Imides.   Nitrides.
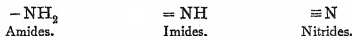
Metal Amides and Amido-Salts.—The most important and most easily prepared of the metallic amides are those of the alkalis and alkaline earths, especially sodamide, $NaNH_2$. These amides are obtained by the action of ammonia on the metals:

$$2Na + 2NH_3 \longrightarrow 2NaNH_2 + H_2,$$
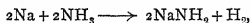
e.g. when the gas is passed into the molten metal decomposition occurs briskly, or the preparation may be carried out by keeping or gently warming solutions of the metals in liquid ammonia. These solutions only decompose slowly, with the evolution of hydrogen, but catalysts such as platinum, iron oxide or even asbestos fibres expedite the decomposition very considerably.

These amides are solid white substances, some of which melt unchanged ($NaNH_2$, m.pt. $210°$; KNH_2, $338°$); they sublime at high temperatures *in vacuo* giving crystals, but at a dull-red heat decompose into their elements. For this reason they are very strong reducing agents in the fused state. The salts and oxides of heavy metals are easily reduced by them to metals, many with violent explosion. They also behave as dehydrating agents, and it is to this property that they owe their employment in organic technology (indigo manufacture). This withdrawal of water depends on hydrolysis, which easily occurs:

$$NaNH_2 + H_2O \longrightarrow NaOH + NH_3.$$
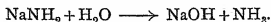
The similarity between the alkali amides and the alkali hydroxides is also shown in their marked dissociation. Not only are they good conductors of electricity when fused,[1] although less so than NaOH, but their solutions in liquid ammonia are also ionised, *e.g.* one containing 0·14 per cent. $NaNH_2$ has only forty-five times the resistance of an equally concentrated aqueous solution of sodium hydroxide. They certainly contain Na and NH_2 ions. Attempts have been made to apply this ionisation to the preparation of hydrazine, $H_2N\text{-}NH_2$. According to Wöhler, this is unsuccessful because the sodamide still present is a powerful catalyst for the decomposition of the hydrazine. On electrolysis, therefore, only ammonia and nitrogen are obtained. Further, hydrazine

[1] Wöhler, *Z. Elektrochem.*, 1918, 24, 261.

cannot be obtained by removing the sodium chemically from the $NaNH_2$. Bromine, iodine or sulphur, which seem most suitable for this, bring about a far-reaching decomposition; in solutions of liquid ammonia a compound Na_2NI_5 is formed with iodine.[1] However, the ionisation of these amides is well shown by decomposition with metallic salts in solution in liquid ammonia, especially by potassamide, which is more easily soluble in ammonia than the others. In this way metallic amides, imides or nitrides are formed as ammonobases (corresponding to the oxybases—hydroxides, oxides, and basic salts—formed on hydrolysis):

Oxybases . . $MR + NaOH \rightleftharpoons M(OH) + NaR$
Ammonobases . $MR + NaNH_2 \rightleftharpoons M(NH_2) + NaR$
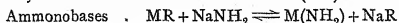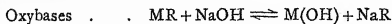
of which those of silver, lead, mercury and bismuth are known[2]:

$$AgNO_3 + KNH_2 \longrightarrow AgNH_2 + KNO_3,$$
$$Pb(NO_3)_2 + 2KNH_2 \longrightarrow PbNH + 2KNO_3 + NH_3,$$
$$3HgI_2 + 6KNH_2 \longrightarrow Hg_3N_2 + 6KI + 4NH_3.$$
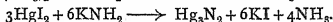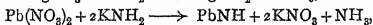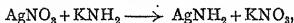
These heavy metal amides, imides and nitrides are generally coloured and are exceptionally explosive. The explosive compounds are obviously different from the ordinary very stable metal nitrides which are described on p. 630. On the other hand, zinc amide is non-explosive, and is formed by an interesting ammonolysis from ammonia gas and zinc ethyl in indifferent solvents[3]:

$$Zn(C_2H_5)_2 + 2NH_3 \longrightarrow Zn(NH_2)_2 + 2C_2H_6.$$
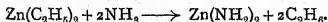
Zinc amide is soluble in liquid ammonia containing potassamide, just as zinc hydroxide is soluble in aqueous potash:

$$Zn(NH_2)_2 + 2KNH_2 \longrightarrow Zn(NHK)_2 + 2NH_3.$$
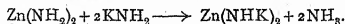
From $TiCl_4$, $NTiNHK$ is obtained, and Mo and W halides yield $NMo(NHK)_2$ and $NW(NHK)_2$.

An ionisation for ammonia, similar to that for water, may, therefore, be postulated:

$$2NH_3 \rightleftharpoons (HNH_3)^+ + NH_2^-; (H.NH_3)^+ \rightleftharpoons NH_4^+ \rightleftharpoons NH_3 + H^+$$
$$2H_2O \rightleftharpoons (H.H_2O)^+ + OH^-; (H.H_2O)^+ \rightleftharpoons H_3O^+ \rightleftharpoons H_2O + H^+.$$
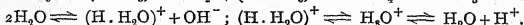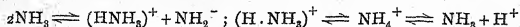
Those substances which dissolve in liquid ammonia to give NH_4^+ ions will be acidic, those which give NH_2^- ions will be basic. Thus Li and NH_4Cl in liquid ammonia react as follows: $2Li + 2NH_4Cl \rightleftharpoons 2LiCl + 2NH_3 + H_2$, and lithium and ammonium sulphide likewise produce lithium sulphide.

There is complete analogy between the action of OH′ ions in

[1] Ruff, *Ber.*, 1900, 33, 3025.
[2] Franklin, *Z. anorg. Chem.*, 1905, 46, 1.
[3] Frankland, *Phil. Mag.* [4], 1857, 15, 149.

hydrolysis and that of NH_2' ions in ammonolysis. Just as the hydrolysis of bismuth chloride to the basic oxychloride is repressed by the addition of hydrochloric acid :

$$BiCl_3 + 2H_2O \rightleftharpoons (OH)_2BiCl + 2HCl,$$
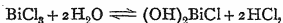
so a similar phenomenon occurs in ammonolysis, *e.g.* of mercuric chloride :

$$HgCl_2 + 2NH_3 \rightleftharpoons NH_2 . HgCl + NH_4Cl.$$
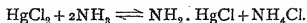
For a summary of the reactions in liquid ammonia, see Audrieth, *Z. angew. Chem.*, 1932, **45**, 385 ; Eméleus, *Ann. Rep. Chem. Soc.*, 1939, **36**, 135.

Mercury Amido-Compounds.—When water is also present, so that hydrolysis and ammonolysis proceed concurrently, only the former is noticed in most metallic salts. Ammonolysis of the halogen compounds of bivalent mercury is particularly common, possibly in accordance with their smaller electrolytic dissociation, but probably also on account of a special affinity between mercury and nitrogen. If dilute ammonia is added to an aqueous solution of corrosive sublimate, $HgCl_2$, there is no trace of hydrolysis, but only an ammonolysis which stops at the ammono-basic salt $Cl . Hg . NH_2$ (*infusible white precipitate*), as shown in the above equation. Further elimination of NH_4Cl takes place[1] in presence of a large excess of ammonia :

$$2Cl . Hg . NH_2 + H_2O \rightleftharpoons Hg:N . Hg . Cl . H_2O + NH_4Cl.$$
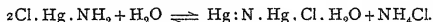
The reaction does not go further with the elimination of the whole of the chlorine, on account of the insolubility of the product. The very sparing solubility of the infusible precipitate makes it a delicate test for bivalent mercury.

Ammine formation or simultaneous ammonolysis and hydrolysis occurs by the action of ammonia on the better dissociated mercury salts of oxyacids. Such ammines[2] as $[Hg(NH_3)_4](NO_3)_2$ and $[Hg(NH_3)_4]S_2O_8$ can be obtained, but binucleate basic salts are usually obtained which are half hydrolysed and half ammonolysed : $X . Hg-O-Hg . NH_2$. They are derived from $HO . Hg-O-Hg . NH_2$ (which is also formulated $HO . Hg . NH . Hg . OH$), the so-called *Millon's base*, which may be made directly by digesting yellow mercury oxide with aqueous ammonia : its numerous salts are related to mercuric oxide, as shown by their colour, which is generally yellow. Basic salts are always intermediate in colour between the oxide or hydroxide and the normal salt. The chloride of Millon's base, $Cl . HgO . HgNH_2$, can also be prepared from mercuri-amido chloride, $ClHg . NH_2$, if this salt is heated with water for a long time ; further hydrolysis then takes place gradually. On boiling with ammonium chloride it is again converted to $ClHg . NH_2$, since in the

[1] Francois, *Ann. Chim.*, 1932, x., **17**, 254.
[2] Fichter and Stern, *Helv. Chim. Acta*, 1928, **11**, 754 ; Weitz, Blasberg and Wernicke, *Z. anorg. Chem.*, 1930, **188**, 344.

presence of NH_4 ions, OH ions are removed; here an exceptionally small amount of NH_3 is sufficient to replace hydrolysis by ammonolysis.

Millon's base contains water of crystallisation, which may be removed by careful dehydration in a current of ammonia. It then forms a brown powder, which on heating to a higher temperature gives up another molecule of water, at the same time losing its basic properties; this dehydration product may be represented by the formula

$$O{\overset{Hg}{\underset{Hg}{\diagdown\diagup}}}NH.$$
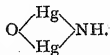
It is very explosive, and its properties are somewhat like those of fulminating gold (*cf.* p. 467); it owes its explosive character to the simultaneous presence of labile oxygen and hydrogen.

The best known salt of Millon's base is the iodide $I . HgOHg . NH_2$, the formation of which from Nessler's reagent forms the most delicate test for ammonia; Nicholls and Willits[1] consider that the composition is $NH_2 . Hg_2I_3$. Nessler's reagent is a solution in caustic potash of the complex compound $K_2[HgI_4]$ or $K[HgI_3 . H_2O]$, which is present in solutions of mercuric salts containing excess potassium iodide. In its preparation, mercuric chloride solution is decomposed with potassium iodide, when insoluble red HgI_2 is precipitated at first, and then dissolves to give a clear solution on the addition of more potassium iodide; potassium hydroxide is then added. This solution indicates the smallest traces of ammonia or ammonium salts by the appearance of a brownish-yellow coloration. With somewhat larger quantities a yellowish-brown, turbid, colloidal liquid is formed after a time, more quickly on warming; in the presence of considerable quantities of ammonia, or on standing, this deposits the iodide of Millon's base as a brown powder. The extraordinarily low solubility of the compound is certainly due to the formation of an internal complex, which has been formulated:

$$O{\overset{Hg-NH_2}{\underset{Hg-I}{\diagdown\diagup}}} \quad \text{or} \quad {\overset{O-Hg-NH_2}{\underset{Hg-I}{\mid}}}$$
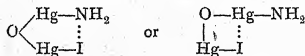
Fusible white precipitate, $HgCl_2 . 2NH_3$, and similar compounds belong to quite another class of mercury-nitrogen compounds, though they are generally related to the ammonobasic mercury salts (infusible precipitate) and the oxyammonobasic ones (Millon's base). The fusible precipitate is a true ammine of mercuric chloride $[Hg(NH_3)_2]Cl_2$. It is formed by the action of ammonia on mercuric chloride if the conditions are such that the ionisation of NH_3 into NH_2' and $H\cdot$ is diminished, *e.g.* if liquid ammonia is allowed to act on $HgCl_2$ or if the gas is used, in the presence of solvents which lessen dissociation (organic liquids). It is also formed in aqueous solution by the action of ammonia on $HgCl_2$ in the presence of a good deal of ammonium

[1] *J. Amer. Chem. Soc.*, 1934, 56, 769.

chloride. No precipitate separates, but the solution crystallises on cooling or concentration. The non-appearance of a precipitate of $NH_2.HgCl$ under these conditions can be understood, since the ammonolysis of $HgCl_2$ is a reversible process:

$$HgCl_2 . 2NH_3 \rightleftharpoons ClHg . NH_2 + NH_4Cl.$$
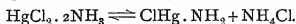
On dilution with water a precipitate of $Cl.HgNH_2$ is formed. In accordance with its nature as an ammine the fusible precipitate may be freed from ammonia by heating. It is remarkable that the corresponding iodide loses its ammonia more easily than the chloride, while in ammines of the type $[M(NH_3)_6]X_2$ the iodides are more stable than the chlorides. Possibly in the fusible precipitate the ammonia and the iodine are in the first sphere—an addition compound (I.) appears:

$$\text{I.} \quad \left[Hg\frac{I_2}{(NH_3)_2}\right]. \qquad\qquad \text{II.} \quad \left[M(NH_3)_6\right]I_2,$$

while in the other compounds the iodine is in the second sphere, thus giving an ionised compound. According to a rule which is generally valid the stability relationships between addition compounds are exactly the reverse of the corresponding ionised compounds.[1]

Other mercury-nitrogen compounds are connected with the ammono-basic salts, and are formed by further ammonolysis of them. Mercuric salts, on hydrolysis, finally yield mercuric oxide; the end-product of ammonolysis, the nitride, is exactly analogous:

$$HgCl_2 + 2KOH \longrightarrow HgO \qquad\qquad 3HgI_2 + 2KNH_2 \longrightarrow Hg_3N_2.$$

To attain this end, and to eliminate hydrolysis completely, the reaction must be carried out in solution in liquefied ammonia. The nitride is then obtained as a voluminous chocolate-coloured substance which is highly explosive: it explodes especially violently on contact with water. With excess of mercury salts, the pure ammono-base, the nitride, is not formed, but yellow ammonobasic salts such as $Hg:N.HgI$ or $Hg:N.HgBr$, just as, when oxybases are added to excess of salts, the basic salt separates instead of the oxide.[2]

Interesting reactions also occur between ammonia and mercurous salts.[3] With concentrated ammonia, the end-product is a grey solid of composition $Hg + NH_2HgCl$, together with the soluble $HgCl_2.2NH_3$ which decomposes as described above. With dilute ammonia a slow reaction yields Hg_2O and NH_4Cl. Hence under ordinary conditions with moderate concentrations, the reaction approximates to the following:

$$2Hg_2Cl_2 + 4NH_4OH \longrightarrow Hg + HgO + NH_2HgCl + 3NH_4Cl + 3H_2O.$$
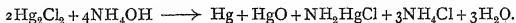
These ammonolytic reactions are especially easy to carry out with mercury salts, but they can also be obtained to some extent with other metals. Similar compounds can be prepared from various

[1] Ephraim, Ber., 1915, 48, 628.   [2] Franklin, Z. anorg. Chem., 1905, 46, 1.
[3] Frecke and Sneed, J. Amer. Chem. Soc., 1938, 60, 518.

metals, such as lead, bismuth, aluminium, silver, antimony, etc., by decomposing solutions in liquid ammonia with potassium iodide; aqueous ammonia acts on them hydrolytically by virtue of its hydroxyl ions. Only bivalent and not univalent mercury has this affinity for nitrogen; mercurous compounds under these conditions yield a mixture of the mercuric complex and free mercury. Mercury is likewise distinguished by a similar tendency to form compounds with carbon.

These mercury compounds are formed not only with ammonia itself, but with substituted ammonias. The substituents may be organic residues or inorganic radicals. To give a single example: mercury replaces the imidohydrogen in imidodisulphonic acid, $HN:(SO_3H)_2$ (cf. p. 641), with the formation of such stable compounds that the metal cannot be removed by treatment with acids.

Metal Nitrides. — Besides the very explosive nitrides there is another large class which are often very stable. Their fomulae are mainly derived from the replacement of all the hydrogen atoms in ammonia by the metals in their normal valency, in contrast to some carbides, borides, etc., and the position of the metal in the periodic system may therefore be determined from them. Only the most noble metals fail to give nitrides, and those of the alkali metals (except lithium) have not been prepared pure, although they have not lacked investigation. Some of the metals of medium affinity do not apparently form nitrides, e.g. tin, but the formation of Ni, Co, Al and Be nitrides is catalysed by lithium nitride, and in other cases sodium fluoride is an effective catalyst.[1]

It is curious that many nitrides contain only one metal atom and one nitrogen atom even when the metal does not belong to the third group of the periodic system. This occurs, for example, in the nitrides of titanium, zirconium, niobium, tantalum and vanadium. The tervalency of these metals, however, plays a small part in these compounds which are non-polar, as can be seen from a consideration of their space lattices.

The preparation of the nitride can be carried out in two main ways: (1) by heating the amides, which give off ammonia at higher temperatures: $3Ba(NH_2)_2 \longrightarrow Ba_3N_2 + 4NH_3$. This method is analogous to the preparation of oxides by heating the hydroxides. It can be used only for the nitrides of the few metals which form true amides, i.e. the alkaline earths and zinc, but not for the amides of the alkali metals, though the thermal decomposition of azides may be used instead.

(2) The nitrides can be prepared synthetically from their constituents, the metal and nitrogen. With the alkali metals it is necessary to make use of active nitrogen obtained by means of a glow discharge, and even then the yield of nitride is extremely small, the azide being principally produced. With other metals nitrogen itself may be used, or it may be liberated nascent during the process by heating the metal with ammonia.

[1] Neumann and Kroger, *Z. anorg. Chem.*, 1931, **196**, 65; 1932, **204**, 81; **207**, 133, 145; 1934, **218**, 379.

The hydrogen which is formed protects the metal from oxidation, and the nitrogen is specially reactive. Very often, however, even metals which are easily oxidised (alkaline earths, magnesium, aluminium) have such a great affinity for nitrogen that they react with it even in the presence of some oxygen (e.g. in air). Thus magnesium and aluminium nitrides may be obtained fairly pure by heating the metal in a limited supply of air. The granulated metal is heated in a crucible closely covered with asbestos, through which a hole is made with a pin. When a certain temperature is reached the reaction is completed with the appearance of a bright glow and an inrush of air from outside. The oxygen then has little action, and the metal becomes converted into pure nitride, which is only covered on the surface with a thin white film of oxide. It is remarkable that the reaction is facilitated by the addition of a little carbon; this element forms a better reducing agent in the presence of nitrogen than when alone, when it tends to escape as carbon monoxide. Nitrides of the metals of the third, fourth and fifth groups can be made in this way and also that of beryllium, but not those of other metals of the first and second groups. As nitrides of metals of the sixth group are dissociated at the temperature reached in this method, they cannot be made synthetically. Carbides, moreover, form nitrides by a strongly exothermal reaction when they are heated in a stream of nitrogen.

Some metals, like lithium and calcium, combine slowly with nitrogen at ordinary temperatures. It is better, however, to induce reaction by local heating; it then proceeds, both in those metals and in magnesium, in the stream of nitrogen from the point of heating, like a combustion in oxygen. If the nitrogen is concentrated the reaction takes place very violently, e.g. when a mixture of liquid nitrogen and magnesium is lit with a fuse.

If ammonia, which acts as a reducing agent at the same time, is used, the nitride is also produced from a compound which can be reduced by hydrogen. Thus copper oxide gives a nitride easily on heating in a stream of ammonia at 300°, and the chlorides of molybdenum, tungsten, uranium, etc., are also converted into nitrides on heating with ammonia. The use of chlorides of metals which are not too difficult to reduce does not hinder the reaction, so that many metallic compounds may be converted into nitrides by roasting with ammonium chloride. Ammonium vanadate, NH_4VO_3, on heating in the absence of air, yields VN by auto-reduction and -oxidation.

The nitrides are gradually converted to the oxides when roasted in air. Hydrolysis assists this process, for atmospheric moisture is especially effective at the high temperature of calcination, e.g. the hydrolysis: $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + 2NH_3$ of the nitrides is an important method for the preparation of ammonia (p. 608). It proceeds at very different rates with different nitrides. Many are

decomposed by atmospheric moisture on keeping in air, and therefore smell of ammonia, changing into the hydroxides in a short time. To these belong the nitrides of the alkaline earth metals, Mg, Zn, Al, etc., while, e.g., Mn_3N_2 or W_2N_3 are only slowly attacked by water, and chromium nitride, CrN, is not decomposed by water at 220°. Decomposition is favoured by caustic alkalis, which, however, only slowly attack zirconium nitride. Acids generally act as better solvents than water, but the ammonia then forms an ammonium salt.

The colours of the nitrides are variously described. Those of metals which usually give colourless compounds are often described as dark brown, green or blackish, but this colour is probably due to impurities. Nitrides purified by sublimation are often white. They form small, clear, transparent crystals.

The nitrides, like the oxides, sublime and fuse only at high temperatures. Many, such as those of Al, Be, Sc, Ti, Zr, V, Nb and Ta, melt between 2000° and 3000°; calcium nitride has the lowest melting point at 900°. Others are very resistant to heat, and their decomposition into the metal and nitrogen takes place with difficulty just as the base metal oxides split up with difficulty into metal and oxygen. The nitrides of the more noble metals naturally decompose more readily; thus copper nitride decomposes above 300° and, on being heated rapidly, gives feeble explosions. These nitrides are difficult to reduce, even in the presence of hydrogen, e.g. chromium nitride even at 560° under 13 atm. pressure undergoes no change; if the metal forms hydrides, decomposition is facilitated; e.g. calcium nitride is converted into its hydride by a reversible reaction with hydrogen at 600°. Gallium nitride, GaN, sublimes without decomposition above 800°.

Complex nitrides are known and a double nitride of lithium and iron, $Li_3N.FeN$ or Li_3 $[Fe^{III}N_2]$ has been investigated.[1] This compound is particularly interesting owing to the use of iron as a catalyst in the synthesis of ammonia, when the formation of a nitride of iron as an intermediate compound may be supposed to take place. Now nitrogen and iron alone do not form a nitride, the compound Fe_2N being produced by the action of ammonia on the metal; but when mixed with either lithium or lithium nitride, Li_3N, the double nitride is formed. It is readily hydrolysed, giving black ferric oxide—not the hydroxide.

Metal Phosphides, Arsenides and Stibides.—As in ammonia, a gradual substitution of the hydrogen in phosphine, PH_3, by metals takes place (and possibly also in arsine), and again the alkali compounds of this class are best known. The deep blue solutions of the alkali metals in liquid ammonia are decolorised when PH_3 is passed in, and a highly refractive liquid resembling carbon disulphide is formed, from which white needles of the phosphides KPH_2 or $NaPH_2$ are deposited when the ammonia is evaporated. They lose PH_3 on

[1] Frankenburger, Andrussor and Dürr, Z. Elektrochem., 1928, 34, 632.

warming and are converted into metallic phosphides free from hydrogen : $3KPH_2 \longrightarrow PK_3 + 2PH_3$.

Similarly, on passing AsH_3 into a solution of metallic calcium in ammonia, an orange liquid is formed from which a lighter coloured precipitate containing ammonia separates, to which is given the formula Ca_3As_2,AsH_3,NH_3. It is converted to Ca_3As_2 on heating *in vacuo*.

The number of phosphides and arsenides which do not contain hydrogen is much larger. They have only a limited resemblance to the nitrides, and, with the exception of those of the alkalis and alkaline earths, they tend to resemble intermetallic compounds. The formulae, for instance, do not always correspond to the usual valencies of the elements, and are often very varied. As examples, the formulae of the phosphides of tin, copper, silver and platinum are given :

Sn_5P_2	Sn_2P	Sn_3P	SnP	SnP_2	Sn_4P_3	SnP_3
Cu_3P	Cu_5P_2	Cu_2P	Cu_3P_2	CuP	CuP_2	...
AgP	Ag_2P_3	AgP_2	Ag_2P_5	...	...	...
Pt_2P	PtP	Pt_3P_5	PtP_2	...	...	...

Many of the metallic phosphides described in the literature are certainly decomposition products and not definite substances. The critical methods employed in recent times for the examination of inter- metallic compounds have not yet been extended to the phosphides. They have, however, already been applied to the arsenides and anti- monides (stibides) of the heavy metals ; these compounds will be more fully described in the consideration of alloys (pp. 856 *ff.*), since they have the character of purely metallic compounds. Their chemical relationship to the phosphides and nitrides is shown by the evolution of arsenic and antimony hydrides on hydrolysis. These alloys are simply prepared by fusing arsenic or antimony with the other metal ; zinc, tin and iron arsenides are used in the preparation of arsine, and calcium and magnesium antimonides for stibine. The precipitates formed in the wet way by dropping salt solutions into AsH_3 have not been proved to be arsenides. The fact that they give arsine on treatment with acids is not conclusive, owing to the finely divided form of the precipitate.

Phosphides can be prepared in three ways : by the action of elementary phosphorus preferably as vapour on the metal, by causing the solid mixture to react with a fuse, or by reducing the phosphate of the metal by means of carbon, best in the electric furnace, *e.g.* : $Ca_3(PO_4)_2 + 8C \longrightarrow Ca_3P_2 + 8CO$. The phosphides prepared by the latter methods are appreciably resistant to heat, but those of the more noble metals can always be decomposed by heat ; there is a reversible reaction,

Metal phosphide $\rightleftharpoons$ Metal + Phosphorus vapour,

which has been evaluated for silver and copper phosphides at various temperatures.[1] For AgP_2 at 605° the equilibrium pressure is 94 mm.,

[1] Granger, *Ann. Chim. Phys.*, 1901 (7), 14, 5.

and for CuP at 570°, 214 mm. Phosphides of baser metals are much more resistant to heat; thus calcium phosphide is not reduced by hydrogen even at 900°. They fuse only with difficulty and, with the exception of zinc phosphide, do not sublime.

There seem to be two distinct classes of phosphides: those which undergo hydrolysis and those which do not. These may be partially distinguished externally. The latter have a metallic appearance, while the former are non-metallic. An explanation of this has already been given for the nitrides. There is, however, no sharp demarcation, for the classes are joined together by transitional phosphides. The more noble the metal the less the phosphide tends to hydrolyse. While the phosphides of the alkaline earths, of magnesium and aluminium, are easily decomposed in a similar way to the nitrides: $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$, others are hardly attacked even by dilute acids. Those which are difficult to attack are metallic, lead grey to silvery white, and blackish when the phosphorus content is high. Those which may be hydrolysed, however, are red to brown, and form hard, brittle crystalline masses.

The phosphides can be kept in dry air. Oxygen attacks them only at higher temperatures with the formation of oxides, and carbon converts them into carbides in the electric furnace. Chlorine alone reacts easily with them at a slightly elevated temperature.

The properties of the phosphides of heavy metals being like those of alloys, they can easily be mixed with other metals or alloys. The mechanical properties of the metal are very strongly influenced by the presence of phosphorus, sometimes in a favourable sense (phosphor-bronze) and sometimes unfavourably (iron, which shows cold-shortness owing to phosphide content). In order to free it from admixed phosphide air is forced into the molten iron in the Bessemer converter. The carbon, silicon and manganese in it burn before the iron itself; oxidised iron is reduced by the carbon added as spiegel or ferro-manganese. The combustion of phosphorus cannot take place in this process unless something is added, since the products of combustion become reduced again by the iron present, at least when the melt is "acid," *i.e.* contains silicic acid:

$$P_2O_5 + Fe + SiO_2 \longrightarrow FeSiO_3 + P.$$
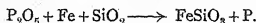
If, on the other hand, the phosphorus pentoxide formed is fixed by the addition of lime or when the converter is basic lined with highly fused magnesia, the phosphorus is completely withdrawn from the iron on combustion (Thomas's Process), being converted into calcium phosphate, which finds useful application in agriculture as basic slag.

The nitrides of the non-metals are very diverse in nature and may be divided into several classes. Those of boron, silicon and phosphorus form one extreme and are distinguished by the most extraordinary

stability ; at the other extreme are the nitrogen compounds of oxygen, sulphur, and especially of the halogens, which are endothermic and tend to decompose spontaneously with violence.

Nitrides, etc., of Phosphorus, Boron and Silicon.—These nitrides are closely connected in behaviour with those of the metals. Their formulae, P_3N_5, BN, Si_3N_4, are in agreement with the usual valencies of their elements. Their mode of formation is similar to that of the metallic nitrides, viz., either by elimination of ammonia on strongly heating amides :

$$B(NH_2)_3 \longrightarrow BN + 2NH_3 \qquad 3Si(NH_2)_4 \longrightarrow Si_3N_4 + 8NH_3,$$

when the imides are formed as intermediate products (*cf.* p. 636), or directly by igniting the non-metals very strongly in a stream of nitrogen or ammonia. P_3N_5 is obtained in good yield[1] by the interaction of P_2S_5 and ammonia gas. As in the formation of metallic nitrides, ammonium salts (NH_4Cl) can also be used in place of ammonia, and the free oxides (B_2O_3 and even borates), chlorides or sulphides instead of the free elements. The compounds are simultaneously reduced and nitrogenated by the decomposition of the ammonia. Nitrogen phosphide obviously cannot be made by methods involving heating owing to the volatility of phosphorus.

These nitrides are probably highly polymerised products. They all form light white powders which decompose only at high temperatures. Phosphorus nitride, P_3N_5, is split up into its components *in vacuo* at bright red heat ; boron nitride, BN, gives an equilibrium dissociation pressure of 158 mm. at 2045°, and Si_3N_4 gives 5·5 mm. at 1529°. BN, if it contains some B_2O_3, exhibits strong phosphorescence on ignition, or after exposure to light.[2] This phosphorescence takes place only in presence of a small quantity of aromatic hydrocarbons, while an admixture of heavy metal salts, which act as stimulants to the luminous sulphides described on p. 536, is quite ineffective with this compound. Boron nitride forms six-sided tabular crystals when heated to a very high temperature and then resembles graphite in colour and other properties. The revelation of its crystal structure by the X-ray method confirms the similarity in build of these two substances. The electron shells present in BN (*i.e.* $5+7=12$) show a close relationship with $2C (=12)$. These nitrides are difficultly fusible (Si_3N_4, m.pt. 1900° ; BN, m.pt. 3000°) and do not dissolve in any solvent without decomposition. They are hydrolysed by water only with very great difficulty, but always give traces of ammonia on boiling, or greater quantities on heating in a bomb-tube to a few hundred degrees. The higher the temperature to which they have previously been heated the more difficult it is to decompose them. Dilute acids or alkalis do not

[1] Stock and Hoffmann, *Ber.*, 1903, 36, 314.
[2] Tiede and Büscher, *Ber.*, 1920, 52, 2206.

decompose them any better, and KOH decomposes them with evolution of ammonia only when they are fused with it. On ignition in hydrogen they are not attacked, and only with difficulty on ignition in chlorine. They are thus among the most refractory substances.

The intermediate products, richer in ammonia, and from which they are formed on heating, are more easily attacked. These substances, amides, imides and similar compounds, are formed from the addition compounds of ammonia with the halides of phosphorus, boron and silicon. At low temperatures ammonia does not decompose these halides, but forms complex compounds, such as $PCl_3, 5NH_3$; $PCl_5, 8NH_3$; $SiCl_4, 6NH_3$; $TiCl_4, 8NH_3$; etc., which give up only hydrogen chloride on heating. Sulphides also form such addition compounds with ammonia, some giving intermediate products such as :

$$SiS(NH_2)_2 \qquad\qquad HN = P(SNH_2)_3$$
Silico-thiourea.   Ammonium imido-trithiophosphate.
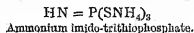
which then yield nitrides or amides on heating, with elimination of ammonia and hydrogen sulphide.

The first products of decomposition, the amides :

$$P(NH_2)_3 \qquad B(NH_2)_3 \qquad Si(NH_2)_2NH,$$
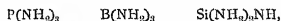
are obtained only at low temperatures, the silicon compound being analogous to guanidine. They are amorphous, the phosphorus compound being yellow, the others white, and even at $0°$ they are converted to the imides :

$$2P(NH_2)_3 \longrightarrow P_2(NH)_3 + 3NH_3 \qquad 2B(NH_2)_3 \longrightarrow B_2(NH)_3 + 3NH_3$$
$$Si(NH_2)_2NH \longrightarrow Si(NH)_2 + NH_3.$$
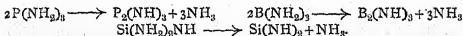
$PN(NH_2)_2$ is obtained by the interaction of $PNCl_2$ and liquid ammonia.

These imides, in contrast to the nitrides, are easily hydrolysed, and boron imide, for example, froths on moistening with water, evolving quantities of ammonia. They give up further quantities of ammonia more or less easily on heating, and are converted into products which are intermediate between the imides and the nitrides. Only boron imide decomposes at $130°$ directly into ammonia and boron nitride ; phosphorimide, formed from phosphorus halides and ammonia, reaches constant weight on heating to $250°$ and then has the formula $N \equiv P = NH$ i.e. : $\overset{=}{N} :: \overset{+}{P} :: \overset{..}{N} : H$ or $N \rightleftharpoons P = N - H$, (phospham), while silicon imide is stable up to $900°$ and is then transformed to a compound of the formula Si_2N_3H. This is stable up to $1300°$ and then decomposes, leaving a residue of silicon nitride, Si_3N_4. The imides are light white powders ; silicon imide is easily hydrolysed by caustic soda ; phospham, on the other hand, is exceptionally stable, and does not give up ammonia on treatment with water, acids or alkalis. It is decomposed only by fusing with potash or by concentrated oxyacids, on which it acts as a reducing agent. If it is heated at $400°$, pure P_3N_5 is produced ($3PN_2H \longrightarrow P_3N_5 + NH_3$), and if heated in vacuo at $730°$, PN sublimes.[1] P_4N_6 is obtained by the interaction of PCl_3 and liquid ammonia.[2]

On account of the high valency of silicon, other compounds containing nitrogen can be obtained by treating chlorinated silanes with ammonia as follows :

$$SiH_3Cl \overset{NH_3}{\longrightarrow} (SiH_3)_3N \text{ and } (SiH_3)_2NH,$$ the former product being a spontaneously inflammable liquid of boiling point $52°$, while the latter polymerises very rapidly to a white powder.

[1] Moureu and Rocquet, Compt. rend., 1934, 198, 1691 ; Bull. Soc. chim., 1936, v, 3, 1801.   [2] Moureu and Wetroff, Compt. rend., 1935, 201, 1381.

$$SiH_2Cl_2 \xrightarrow{NH_3} SiH_2(NH)$$, which is immediately polymerised to a substance resembling silicic acid.

$$SiHCl_3 \xrightarrow{NH_3} [SiH(NH)]_2NH$$, a solid polymer which loses ammonia at $100°$ and forms SiHN.

$(SiH_3)_3N$ corresponds to trimethylamine $(CH_3)_3N$, but does not form salts. On treatment with hydrochloric acid or other halogen acids it is decomposed thus:
$(SiH_3)_3N + 3HCl \longrightarrow 3SiH_3Cl + NH_3$.

Some compounds of this class contain a "silicon bridge." Thus Si_2Cl_6 gives the amide-imide compound I. at very low temperatures, which at $-10°$ gives a polymerised form of compound II.

$$\begin{array}{c} NH_2 \qquad\qquad NH_2 \\ Si\text{---}Si \\ NH \qquad\qquad NH \\ I. \end{array} \qquad\qquad \begin{array}{c} HN:Si\text{----}Si:NH \\ NH \\ II. \end{array}$$
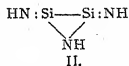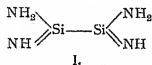
This compound decomposes in turn at $400°$ with loss of ammonia and formation of polymerised silico-cyanogen, Si_2N_2.[1]

$(SiCl)^x$ gives $Si_6(NH_2)_6$ and $Si_8(NH_2)_{10}$ on reaction with ammonia.

$GeCl_4$ forms germanimide, $Ge(NH)_2$ in liquid ammonia; if heated, this gives Ge_2N_3H and Ge_3N_4.

The compound $B_3N_3H_6$ has been shown[2] by X-ray analysis to have the ring structure indicated at the side, so that it is really a hydrogenated boron nitride and is very probably a resonance structure, much like benzene. It is a liquid of b.pt. $53°$, freezing at $-58°$, and is not appreciably decomposed even at $500°$. In this stability it differs from such open chains as $B_2(NH)_3$. It can be made by warming the addition products of ammonia and boron hydrides, for example, $B_4H_{10}\cdot 4NH_3$ (p. 769). The similarity of certain of its physical properties and those of benzene suggest corresponding structures (the electron shells $B+N=2C$ is worthy of note). It reacts with cold water to give a trihydrate (I), which passes to II with hydrogen chloride. $B_3N_3H_6$ with HCl gives $[B_3N_3H_6]Cl_3$, formulated as in III.

$$I$$

$$II$$

$$III$$
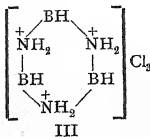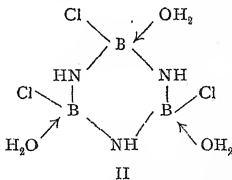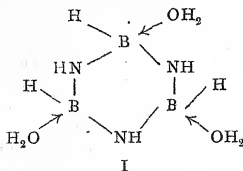
[1] Schwarz and Sexauer, *Ber.*, 1926, 59, 333.

[2] Stock and Wierl, *Z. anorg. Chem.*, 1932, 203, 228.

THE HYDRIDES OF THE ELEMENTS
OF THE FIFTH GROUP (*continued*)

Acid amides—Of nitric acid—Of sulphuric acid—Of sulphurous acid—Of phosphoric acid—Hydrazine and hydroxylamine—Hydrazoic acid, halogen azides— Lower hydrides of phosphorus

Acid Amides

IN ammonia the hydrogen atoms can be replaced either by metals or by negative groups in the same way as in water:

$$\text{I.} \quad \begin{array}{c} H.OH \\ Na.OH \end{array} \quad \text{II.} \quad \begin{array}{c} H.OH \\ NO_2.OH \end{array} \quad \text{I.} \quad \begin{array}{c} H.NH_2 \\ Na.NH_2 \end{array} \quad \text{II.} \quad \begin{array}{c} H.NH_2 \\ NO_2.NH_2 \end{array}$$
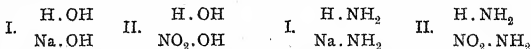
Replacement by metals gives the metal amides (p. 625); while negative groups give the important class of acid amides. They dissociate with formation of hydrogen ions almost as readily as the hydroxy-acids; and another way of regarding their constitution is to look upon them as hydroxy-acids in which one OH group has been replaced by NH_2. This substitution may affect several OH groups one after the other:

$$SO_2 \begin{array}{c} \diagup OH \\ \diagdown OH \end{array} \rightarrow SO_2 \begin{array}{c} \diagup NH_2 \\ \diagdown OH \end{array} \rightarrow SO_2 \begin{array}{c} \diagup NH_2 \\ \diagdown NH_2 \end{array}$$

Sulphuric   Amidosulphonic   Sulphamide.
acid.   acid.
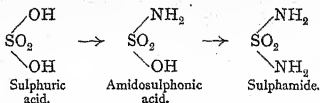
The amido-acids contain both OH and NH_2 groups; in consequence they can be derived only from polybasic acids.

The acid amides can lose ammonia in the same way that hydroxy-compounds lose water to form anhydrides; the products are called imides:

$$\begin{array}{c} SO_2 \diagup OH \\ \diagdown O.H \\ SO_2 \diagup O.H \\ \diagdown OH \end{array} \xrightarrow{-H_2O} \begin{array}{c} SO_2 \\ \diagdown O \\ SO_2 \diagup \\ \diagdown O.H \end{array} \xrightarrow{-H_2O} 2SO_3$$

$$\begin{array}{c} SO_2 \diagup NHH \\ \diagdown NH.H \\ SO_2 \diagup NHH \\ \diagdown NHH \end{array} \xrightarrow{-NH_3} \begin{array}{c} SO_2 \\ \diagdown NH \\ SO_2 \diagup \\ \diagdown NH.H \end{array} \xrightarrow{-NH_3} 2SO_2.NH$$

Sulphuric Pyrosulphuric Sulphur   Sulphamide. Imidosulphamide. Sulphimide.
acid.   acid.   trioxide.
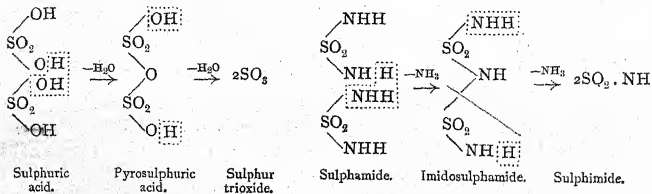
The amides and imides of some of the oxy-acids are not known. The most important are those of nitric, sulphuric, phosphoric and carbonic acids. The amides of silicon and boron described in the last chapter can be regarded as the amides of orthosilicic and boric acids.

Acids can be made by the addition of water to the anhydride, and similarly, amido-acids can be prepared by the addition of ammonia to acidic oxides:

$$O_2S = O + OH \cdot H \longrightarrow O_2S{\large{<}}^{OH}_{OH} \qquad O_2S = O + {}^H_{NH_2} \longrightarrow O_2S{\large{<}}^{OH}_{NH_2}$$

$$\text{Sulphuric acid.} \qquad\qquad\qquad\qquad \text{Amidosulphonic acid.}$$

$$OC = O + {}^H_{NH_2} \longrightarrow OC{\large{<}}^{OH}_{NH_2}$$

$$\text{Carbamic acid.}$$
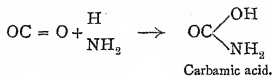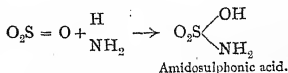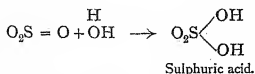
Another way of forming hydroxy-acids is by the hydrolysis of some of their derivatives, particularly of the halogen derivatives; the amido-acids are similarly formed by the ammonolysis of these compounds:

$$O_2S{\large{<}}^{OH}_{Cl+H\ OH} \xrightarrow{-HCl} O_2S{\large{<}}^{OH}_{OH} \qquad O_2S{\large{<}}^{OH}_{Cl+H\ NH_2} \xrightarrow{-HCl} O_2S{\large{<}}^{OH}_{NH_2}$$

$$\text{Sulphuric acid.} \qquad\qquad\qquad\qquad\quad \text{Amidosulphonic acid.}$$

$$O_2S{\large{<}}^{Cl+H\ NH_2}_{Cl+H\ NH_2} \xrightarrow{-2HCl} O_2S{\large{<}}^{NH_2}_{NH_2} \qquad OC{\large{<}}^{Cl+H\ NH_2}_{Cl+H\ NH_2} \xrightarrow{-2HCl} OC{\large{<}}^{NH_2}_{NH_2}$$

$$\text{Sulphamide.} \qquad\qquad\qquad\qquad\quad \text{Carbamide} \atop \text{(Urea).}$$
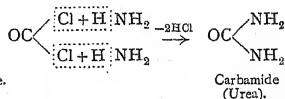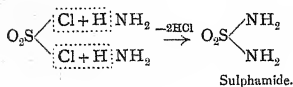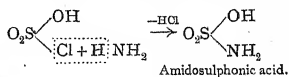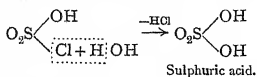
Fluosulphonic acid, $HO.SO_2.F$, which is difficult to hydrolyse, is specially amenable to ammonolysis.[1]

Besides these general reactions, which do not always take place smoothly, there are also special reactions, which often give the product with greater certainty.

Nitramide, $O_2N.NH_2$, the amide of nitric acid, has not so far been obtained by the usual methods. To prepare it the ethyl ester of carbamic acid, urethane, is converted into its nitro-derivative by nitric acid and concentrated sulphuric acid, the latter serving to withdraw the water:

$$OC{\large{<}}^{NH\boxed{H+HO}NO_2}_{OC_2H_5} \xrightarrow{-H_2O} OC{\large{<}}^{NH.NO_2}_{OC_2H_5}$$
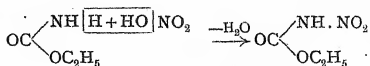
[1] Traube and Brehmer, *Ber.*, 1919, 52, 1284.

The ester is then hydrolysed by caustic potash :

$$OC \begin{array}{l} NH.NO_2 \\ O \overline{C_2H_5} \\ + \\ K \underline{OH} \end{array} \xrightarrow{-C_2H_5OH} OC \begin{array}{l} NH.NO_2 \\ OK \end{array}$$
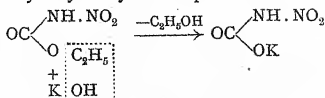
and finally, by hydrolysis with sulphuric acid, the potassium salt breaks down into carbonic acid and nitramide [1] :

$$\begin{array}{l} HO \overline{H + NH.NO_2} \\ OC \\ OH \end{array} \xrightarrow{-H_2CO_3} NH_2.NO_2.$$
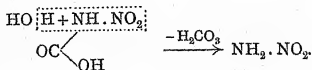
The white leaflets of nitramide, which melt at 75°, are easily soluble in water, alcohol and ether, and the solution gives an acid reaction ; nitramide is, however, a weaker acid than acetic acid. Since it can be reduced to hydrazine, $H_2N.NH_2$, its nitrogen atoms must be directly attached to each other ; the method of union of the oxygen and hydrogen atoms is still in doubt and indeed differs with the medium. It may be supposed that the oxygen and hydrogen in the compound are held together by a residual valency force as well as being attached to the nitrogen, as expressed diagrammatically by formula I. :

$$\text{I.}\; \begin{array}{ccc} H\cdots\cdots O \\ | \quad | \\ N\text{---}N \\ | \quad | \\ H\cdots\cdots O \end{array} \qquad \text{II.}\; \begin{array}{c} H\cdots\cdots O \\ \searrow \quad | \\ N\text{---}N \\ \nearrow \quad | \\ H\cdots\cdots O \end{array} \qquad \text{III.}\; \begin{array}{c} \cdots HO \\ | \nearrow \\ N\text{---}N \\ | \searrow \\ \cdots H.O \end{array}$$
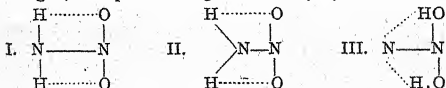
In an acid medium, in the presence of hydrogen ions, the basic (amino) character of the compound comes more to the fore (II.), while in alkaline solution the oxygen and hydrogen tend to combine, with the formation of an acidic compound (III.). In agreement with this, decomposition occurs easily in alkaline media, with liberation of N_2O, which can be explained by loss of water :

$$N.N \begin{array}{l} O \overline{H} \\ OH \end{array}$$
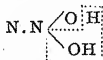
while the compound is fairly stable in acid solution. There are therefore no salts of nitramide, with the exception of a mercury compound, $Hg:N.NO_2$, which exists only on account of the exceptional affinity of mercury for nitrogen, which has been already mentioned.

Nitramide is an isomer of hyponitrous acid, possibly a stereoisomer.

The above formulae may be regarded as stages in the following electronic transitions :

$$\begin{array}{l} H \\ \quad \searrow \\ \quad \overset{+}{N^2}\!\!=\!\!\overset{}{N} \\ H \nearrow \quad \searrow O^4 \end{array} \overset{\overline{O}^6}{\longrightarrow} H\!=\!\!\overset{+}{N^2}\!\!\equiv\!\!\overset{+}{N} \begin{array}{l} O^4\!\!=\!\!H \\ \overline{O}^6 \end{array} \longrightarrow \overline{N}^4\!\!\equiv\!\!\overset{+}{N} \begin{array}{l} O^4\!\!=\!\!H \\ O^4\!\!=\!\!H \end{array}$$
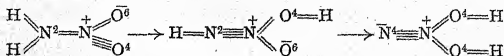
[1] Thiele and Lachmann, *Ann.*, 1895, 288, 267.

but the partial valency conceptions involved in I, II, III, may be expressive of resonance phenomena, which may well be expected in this compound.

Nitrosamine, NH_2NO.—Schwarz and Giese [1] prepared this substance in solution by the interaction of ammonia and N_2O_3 at the melting point of liquid ammonia. On evaporation of the solvent, the orange solution decomposes to ammonium nitrite and nitrogen :

$$2NH_2NO \longrightarrow NH_4.NO_2 + N_2.$$
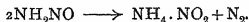
The **amides of sulphuric acid** and related compounds form an extensive and interesting class of substances. All three hydrogen atoms of ammonia can be replaced by the radical $-SO_3H$. They may also be replaced by hydroxyl groups, and finally, the nitrogen can take up oxygen, with increase in valency.

The table on page 643 gives a summary of the most important compounds of this group, which have mostly been investigated by Raschig and Divers.

Besides the reactions considered on p. 638, which lead to the formation of amidosulphonic acid and sulphamide, the action of nitrites on sulphites gives the most important members of this class. According to the method, this reaction may proceed so that all the oxygen is taken out of the nitrous acid, or so that one hydroxyl group still remains in it. In the first case (I.) salts of nitrilosulphonic acid are formed, and in the second (II.) those of hydroxylamine sulphonic acid :
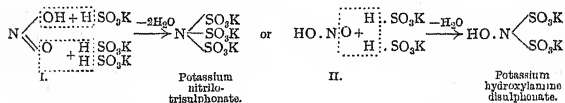
These two parent substances readily undergo hydrolysis in the presence of acids, with removal of sulphonic acid groups :
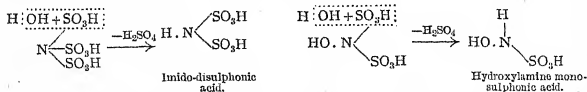
and on further hydrolysis, for which heating with acid is necessary, a second molecule of sulphuric acid is removed, thus :
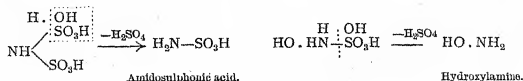
This is one of the best methods of preparing hydroxylamine. The

[1] *Ber.*, 1934, 67, 1108.

amidosulphonic acid can also be broken down into ammonia and sulphuric acid, but prolonged heating with hydrochloric acid to 180° is necessary :

$$\mathrm{H_2N \!:\! SO_2H \longrightarrow NH_3 + H_2SO_4.}$$
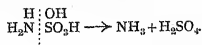
Sulphamic acid is readily prepared from urea and fuming sulphuric acid. It is colourless, non-hygroscopic and crystalline ; in aqueous solution it is highly ionised, forming strongly acidic solutions. Under ordinary conditions, sulphamic acid is practically stable in water, but at higher temperatures it is slowly hydrolysed to acid ammonium sulphate. The salts of sulphamic acid are stable in neutral or alkaline solution, and may be evaporated without hydrolysis of the amino group. All of the known salts of sulphamic acid, with the single exception of a basic mercury salt, are soluble in water. Salts such as lead and barium sulphamate show exceptionally high water solubility.

All these acids, when they can be isolated, are solids and form well-crystallised salts of which those of the alkalis are specially characteristic. In imidodisulphonic acid, $\mathrm{HN \!:\! (SO_3H)_2}$, the hydrogen atom of the imide group may be replaced by metals, and in amidosulphonic acid certain metals can also take the place of the hydrogen. Similar isomers to those of nitramide (p. 639) may be assumed, but they are less pronounced. The existence of these isomers is easily seen from the ease with which the compounds are hydrolysed by H˙ ions in contrast to their marked stability in alkaline solution. While their salts with colourless metal ions are always colourless, the silver salt of amidosulphonic acid is yellow if precipitated from alkaline solution, when the silver always replaces one of the hydrogen atoms of the amido group.

Another series of hydroxylamine sulphonic acids is obtained by the oxidation of potassium hydroxylamine disulphonate, $\mathrm{HO \cdot N(SO_3K)_2}$. Hydroxylamine trisulphonic acid, $\mathrm{(SO_3H) \cdot O \cdot N \!:\! (SO_3H)_2}$, is thereby formed. On hydrolysis the SO_3H residue linked to nitrogen splits off first, while the one attached to the O atom splits off last, so that the following hydrolytic products are formed :

$\mathrm{(SO_3H)O \cdot NH \cdot SO_3H}$ Hydroxylamine iso-disulphonic acid.	isomeric with	$\mathrm{HO \cdot N(SO_3H)_2}$ Hydroxylamine disulphonic acid.
then : $\mathrm{(SO_3H)O \cdot NH_2}$ Hydroxylamine iso-mono- sulphonic acid.	isomeric with	$\mathrm{HO \cdot NH \cdot SO_3H}$ Hydroxylamine mono- sulphonic acid.
then : $\mathrm{HONH_2}$	identical with	$\mathrm{HO \cdot NH_2}$ (Hydroxylamine).

It is also possible by oxidation processes to produce compounds in which the nitrogen behaves as more than tervalent, some being

AMIDES OF SULPHURIC ACID

Unoxidised Derivatives of Ammonia.		H Atoms in the NH₂ Group replaced by OH.		Oxidation gives Quadrivalent Nitrogen.	Constitution unknown.
$H_2N.SO_2.NH_2$ Sulphamide.	$H_2N.SO_2.OH$ Sulphamic acid. Amidosulphonic acid.	$H \cdot N.SO_2.OH$ $HO.$ Hydroxylamine mono-sulphonic acid.	$HO.SO_2.O.NH_2$ Peroxylamine iso-monosulphonic acid.	$HO.N.SO_2.OH$ (?) $O:N.SO_2.OH$ (?) Nitrosisulphonic acid.	$H_2SO_3 . 2NO$ Nitrosylsulphurous acid.
$HN:(SO_2.NH_2)_2$ Imidosulphamide.	$HN:(SO_2.OH)_2$ Imidodisulphonic acid.	$HO.N:(SO_2.OH)_2$ Hydroxylamine disulphonic acid.	$HO.SO_2.O.N\diagdown{}^{H}_{SO_2.OH}$ Hydroxylamine iso-disulphonic acid.	$O:N:(SO_2.OH)_2$ Peroxylamine sulphonic acid.	
$[N:SO.OH]_x$ Sulphomelide. $[HN:SO_2]_3$ Trisulphimide.	$N:(SO_2.OH)_3$ Nitrilosulphonic acid.		$HO.SO_2.O.N:(SO_2.OH)_2$ Hydroxylamine tri-sulphonic acid.	$O_2N.SO_2.OH$ Nitrosulphonic acid.	

of special interest because of their intense colours, as, for example, the compounds:

$$O:N:(SO_3H)_2 \qquad\qquad O:N{<}{\atop\ \ SO_3H}^{\displaystyle OH} \quad (?)$$

Peroxylamine sulphonic acid.   Nitrosisulphonic acid.
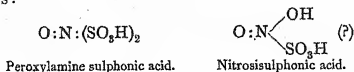
These may contain quadrivalent nitrogen. The former is certainly not stable in the solid state; solid salts of nitrosisulphonic acid are also unknown, and considerable doubt has been thrown[1] on the formulation, due to Raschig, which is given above. Nitrosisulphonic acid is distinguished by its intense blue colour. It is, however, only known in solution, like its salts, of which the cupric, ferrous and mercuric salts in particular are stable, and have a beautiful violet colour. Nitrosisulphonic acid is best formed by the reduction of nitrosulphonic acid, $O_2N.SO_3H$ ("chamber crystals") with sulphurous acid or metals. It is also obtained by the oxidation of hydroxylamine sulphonic acid, $HO.NH(SO_3H)$, by persulphuric acid, and synthetically from sulphuric acid and nitric oxide:

$$ON + SO_3H{\atop}^{\displaystyle OH} \longrightarrow ON{-}SO_3H{\atop}^{\displaystyle OH}.$$
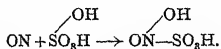
A strong argument against the above constitutional formula is the fact that perchloric acid gives a similar blue-violet compound with nitric oxide, and similar assumption in this case would lead to an extremely improbable formula. Nitrosisulphonic acid is possibly an unstable intermediate product occurring in the lead chamber process (cf. p. 571) Its mercury salt is observed in the use of Lunge's nitrometer for the estimation of the "nitrosyl sulphuric acid content" of a sulphuric acid containing higher oxides of nitrogen. In the nitrometer the sulphuric acid containing nitrogen compounds is shaken with metallic mercury; in that way the oxides of nitrogen are reduced to NO, which is insoluble in sulphuric acid, and the volume of which can be measured in the nitrometer. A small quantity of the NO does not escape, but remains dissolved as the mercuric salt of nitrosisulphonic acid, and gives a pale violet colour to the sulphuric acid. Nitrosisulphonic acid can also take part in the normal test for nitric acid by ferrous salts and concentrated sulphuric acid; sometimes the brown ring, which owes its colour to the complex ferrous ions $Fe(NO)^{..}$, is not obtained, but an amethyst-coloured zone due to the ferrous salt of nitrosisulphonic acid, appears instead, especially at great dilutions. It is also possible to obtain these salts in considerable concentration and a correspondingly intense colour by passing nitric oxide into a solution of cupric or ferrous sulphate in concentrated sulphuric acid. The intense blue coloration is not due to the complex metal-nitric oxide ion.

Peroxylamine sulphonic acid and its salts are formed by the action

[1] Hantzsch and Berger, Z. anorg. Chem., 1930, 190, 332.

of lead dioxide or other oxidising agents on $HO.N:(SO_3H)_2$ in alkaline solution. The hydrogen atom of the OH group is thus removed. The solution thereby becomes an intense dark reddish blue, similar to permanganate. If it is evaporated it deposits the salts contained in it as yellow crystals without becoming decolorised itself; when these crystals are dissolved in water they yield the deep purple solution again. They may also be obtained in solid solution mixed with other crystals, as the blue modification. The compound thus appears in two forms which are in equilibrium with each other in solution, and of which the yellow is more sparingly soluble. As the equilibrium sets in rapidly, the blue form is completely broken up during the separation of the yellow. Compounds containing quadrivalent nitrogen are frequently blue but the molecules may be polymerised forms; it may thus be assumed that the group $O:N$ exists in the blue form, while the yellow contains the group $KO.N:$, but according to the latter formulation no constitutional formula can be evolved which contains only principal valencies. Asmussen[1] showed that the yellow solid is feebly paramagnetic, and the solution shows the strong paramagnetism to be expected of an "odd" molecule; this is in accordance with the equilibrium:

$$[ON(SO_3K)_2]_2 \rightleftharpoons 2(KSO_3)_2NO.$$

Nitrosylsulphuric acid, $SO_3H.O.NO$ (so-called lead chamber crystals), is the most highly oxidised product of this series. (There is little evidence for the existence of the isomeric nitrosulphonic acid $O_2N.SO_3H$ previously supposed to exist; its structure is that of nitracidium sulphate, p. 689.) Nitrosylsulphuric acid is formed by the oxidation of the acids $HO.HN.SO_3H$ or $O:(OH)N.SO_3H$ by persulphuric acid. It is clear from this mode of formation that the nitrogen in it is directly linked to sulphur, and acids may be obtained from it by reduction in which this configuration is preserved. Other reactions, however, cannot be explained on the basis of this constitution, but seem to prove that nitrosulphonic acid is the mixed anhydride of nitrous and sulphuric acids:

$$SO_3H.O\overline{H+HO}NO \xrightarrow{-H_2O} SO_3H.O.NO.$$
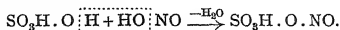
Here the nitrogen would be linked to the sulphur by means of an oxygen atom. The formation of nitrosyl chloride from nitrosulphonic acid and hydrochloric acid is in favour of the latter formula:

$$O_2S{\Large\langle}^{O.\ \overline{NO+Cl}\ H}_{OH} \longrightarrow O_2S{\Large\langle}^{OH}_{OH} + NOCl.$$
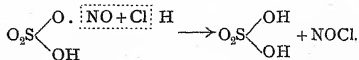
An equilibrium between both forms probably exists. The $O-.NO$ form appears in the solid acid, as indicated by its lack of

colour. A solution in concentrated sulphuric acid, however, has a yellow colour, which would be caused by the nitro form, $-NO_2$. The molecular weight (71·72) of chamber crystals, determined cryoscopically in sulphuric acid, led Hantzsch to the view that the substance is an electrolyte, giving NO^+ and HSO_4^- ions (see p. 683). The conductivity of nitrosyl perchlorate in nitromethane supports the salt-type formulae[1] $[NO]^+[ClO_4]^-$ and $[NO]^+[HSO_4]^-$. The Raman spectra of these substances can only be interpreted on the basis of ionic structures.[2]

Nitrosylsulphuric acid can be formed whenever concentrated sulphuric acid comes in contact with nitrous acid or its anhydride, or when sulphur dioxide reacts with oxides of nitrogen and oxygen in the presence of moisture:

$$SO_4H_2 + 2NO_2 \longrightarrow SO_3H \cdot ONO + HNO_3$$

$$O_2S{\diagdown \atop O} \quad + {NO_2 \atop H} \longrightarrow O_2S{\diagup NO_2 \atop \diagdown OH}$$
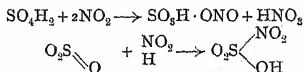
when a compound, $SO_3H \cdot NO$, nitrososulphonic acid, is formed as an intermediate product. This reaction plays a part in the lead chamber process (*cf.* p. 570); when SO_2 and nitrous fumes, with an insufficient supply of moisture, meet in the lead chamber, the white feathery "lead chamber crystals" SO_3HNO_2 are deposited on the walls of the chamber.

A compound of this class, potassium nitrososulphite, K_2SO_3, $2NO$, or $K_2SO_4 \cdot N_2O$ (see p. 667), is formed when nitric oxide is passed into an alkaline potassium sulphite solution. With regard to its constitution, it is known—

1. That the nitrogen must be closely combined with sulphur, since true acids of nitrogen and sulphur, viz. NH_2SO_3H or $HO \cdot NH \cdot SO_3H$, are obtained by suitable treatment.

2. That, on the other hand, the nitrogen may also be split off easily since a sulphate is obtained by treatment with sodium amalgam.

3. That both nitrogen atoms are dependent upon each other, since hydrazine is obtained by reduction with sodium amalgam. The compound decomposes on acidification or on treatment with catalysts (platinum sponge or metallic oxides), with internal oxidation and reduction, giving nitrous oxide and the sulphate.

The constitution is difficult to explain according to these results.[3] The isonitramine formula, $O{\diagup N-OK \atop \diagdown N-SO_3K}$, has been suggested by several workers, and agrees with the reactions of the substance; but no other compound with the NO groups linked in this way is known.

The ammonia derivatives of sulphuric acid, in which both hydroxyl

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[1] Hantzsch and Berger, *Z. anorg. Chem.*, 1930, 190, 321.

[2] Angus and Leckie, *Proc. Roy. Soc.*, 1935, A, 149, 327 ; 150, 615 ; *Trans. Faraday Soc.*, 1935, 31, 958.

[3] For literature, see Divers, *Ber.*, 1905, 38, 1874.

groups are replaced by an amido or imido group, will next be considered. These are generally obtained by the action of ammonia on sulphuryl chloride, when the reaction which ensues depends on which of the reagents is in excess:

$$SO_2 \begin{array}{l} Cl \\ Cl \end{array} + \begin{array}{l} H \\ H \end{array} \begin{array}{l} NH_2 \\ NH_2 \end{array} \xrightarrow{-2HCl} SO_2 \begin{array}{l} NH_2 \\ NH_2 \end{array} \qquad SO_2 \begin{array}{l} Cl_2 + NH_3 \end{array} \xrightarrow{-2HCl} SO_2 : NH$$

Sulphamide.   Sulphimide.

$$NH_2 \begin{array}{l} H + Cl \end{array} . SO_2 . \begin{array}{l} Cl + H \end{array} NH \begin{array}{l} H + Cl \end{array} . SO_2 . \begin{array}{l} Cl + H \end{array} NH_2 \xrightarrow{-4HCl} NH_2 . SO_2 . NH . SO_2 . NH_2$$
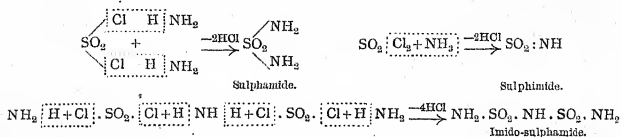
Imido-sulphamide.

The chain formation which leads to imido-sulphamide may even proceed further with the formation of still longer chains. Sulphamide can be obtained free from other products by treating sulphuryl fluoride with ammonia.

All these substances are colourless, crystalline and very easily soluble in water. They can exchange their hydrogen for metal, but the acidic properties of the NH_2 groups are so slight that sulphimide has no noticeable conductivity in water. Like all its homologues, it forms sparingly soluble silver and lead salts; alkali and alkaline earth salts can also be prepared. The imide hydrogen atoms are particularly easily replaced by metal. All these substances easily undergo hydrolysis, when ammonia splits off and amido-sulphonic acid is formed.

The most interesting product of this class is sulphimide, $SO_2 : NH$, which was first obtained as its silver salt.[1] It exists only in the polymerised form in the free state, and in many respects resembles cyanic acid, $CO : NH$, the imide of carbonic acid, which also tends to polymerise. Its polymerisation products, cyanuric acid and gelatinous cyamelide, correspond in appearance and behaviour with trisulphimide and gelatinous sulphomelide.

The following formulae may be given to these substances:

Trisulphimide: I,   or II,

Sulphomelide: III,   or IV,
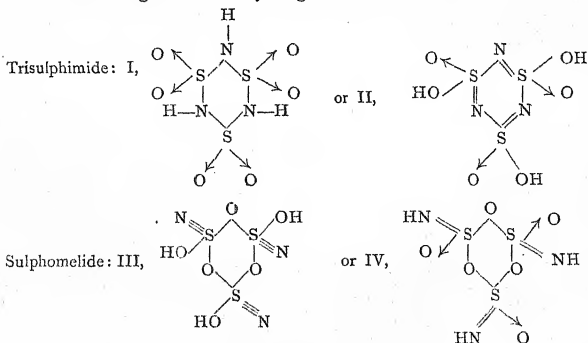
[1] Traube, *Ber.*, 1895, **25**, 2472.

In these formulations, each H atom has a duplet shell, each N an octet; in I, sulphur has a valency shell of 8 electrons, in II and IV, shells of 10 electrons and in III, a shell of 12 electrons.

Nitrosulphamide, $H_2N.SO_2.NH.NO_2$, corresponds to nitramide, and is formed by nitrating sulphamide. It is an explosive solid substance.

Sulphurous acid forms a very similar series of amido-compounds, which have not been studied to such a wide extent. By the action of gaseous ammonia on sulphur dioxide many decomposition products are formed, *e.g.*:

$$NH_2.SO_2H \qquad\text{and}\qquad HO_2S.NH.SO_2H$$

<div style="text-align:center">Amido-sulphinic acid.   Imido-disulphinic acid.</div>
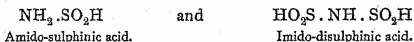
and their ammonium salts. The amide of imido-disulphinic acid, $NH_2.SO.NH.SO.NH_2$, is obtained by the action of ammonia on thionyl chloride.

These imido-compounds are distinguished by the red colour of their salts, especially the silver salts. This is an indication that the nitrogen in them is linked to silver, since this combination always gives rise to vivid colours. Thus:

Silver urethane   .   . $AgHN.CO_2C_2H_5$, is red.

Silver amidosulphonate . $AgHN.SO_3H$, is egg-yellow.

Silver acetamide   .   . $AgHN.CO.CH_3$, is orange, etc.
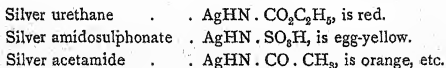
Imino-monopersulphuric acid, H_2SO_4NH, m.pt. 210°, is formed when dry air containing hydrazoic acid is passed into fuming sulphuric acid. On hydrolysis by water this compound forms sulphuric acid and hydroxylamine.

Hydrazine, like ammonia, can exchange its hydrogen for sulphuric and sulphurous acid radicals. The formulae of some of the substitution products, which have hitherto been obtained only in the form of salts, may be quoted:

<div style="text-align:center">HYDRAZIDES OF SULPHURIC ACID</div>

$$HN{-}SO_3H \atop \qquad\quad HN{-}SO_3H \qquad H_2N.NH.SO_3H \qquad SO_2{\nearrow NH.NH_2 \atop \searrow NH.NH_2}$$

<div style="text-align:center">Hydrazido-disulphonic acid.   Hydrazido-sulphonic acid.   Sulphohydrazide.</div>
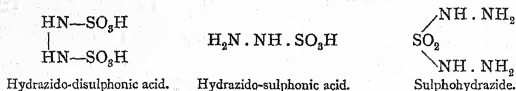
<div style="text-align:center">HYDRAZIDE OF SULPHUROUS ACID</div>

$$NH.SO_2H \atop NH.SO_2H$$
<div style="text-align:center">Hydrazido-disulphinic acid.</div>
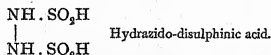
An *azo-compound* is obtained[1] when the pyridine salt of hydrazido-disulphonic acid is oxidised with bleaching powder and potassium chloride added. The yellow, explosive and very insoluble potassium

[1] Konrad and Pellens, *Ber.*, 1926, 59, 135.

salt of azodisulphonic acid separates; it reacts with water with violent evolution of nitrogen, and formation of bisulphite and bisulphate:

$$KO_3S . N = N . SO_3K + HOH \longrightarrow N_2 + KHSO_3 + KHSO_4.$$
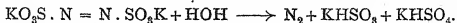
Amides, etc., of Phosphoric Acid.—The number of phosphoric acid amides, imides and nitrides is very great, since the acid is tribasic. Besides this, however, these compounds tend to polymerise in a very interesting manner, as has been noticed in sulphimide alone of the sulphuric acid derivatives; this leads not only to tri-compounds, but to a regular series. Oxidised derivatives corresponding to the nitro- or hydroxylamine sulphonic acids are, however, lacking in the phosphoric acid series.

These substances are prepared by the two general methods used for obtaining inorganic acid amides: the addition of ammonia to the acid anhydride, or double decomposition between the acid chloride and ammonia.

When phosphorus pentoxide is treated with ammonia or ammonium carbonate a variety of products is formed, which are probably the amide and imide of phosphoric acid,[1] but they have not been completely investigated. The products of the action of ammonia on phosphorus chlorides are better known. Mono- or di-chlorophosphoric acid in particular, as well as their phenyl esters, are converted into the amide by ammonia. The phenyl groups may be split off afterwards by saponification with caustic potash:
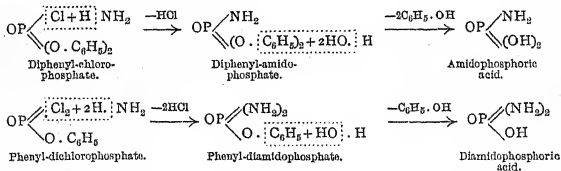
These acids are colourless solids, crystallising in plates or sheets. The monoamido-acid dissolves in water easily, and the diamido-acid less readily. Their salts are also easily soluble, with the exception of the characteristic silver salt. The monoamido-acid is dibasic, but the diamido-acid can be pentabasic, and a silver salt, $Ag_5PN_2H_2O_5$, of it is known,[2] which is distinguished by its explosive properties.

All other attempts to prepare amidophosphoric acids lead to polymerised substances. The products of the action of phosphorus pentachloride on ammonium chloride are of especial interest,[3] as a whole series of homologues may be isolated. Various isomers of the formula $(PNCl_2)_x$, phosphorus chloronitride, are first obtained, which

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[1] Mente, *Ann.*, 1888, 248, 244. [2] Stokes, *Ber.*, 1894, 27, 565.
[3] Stokes, *Amer. Chem. J.*, 1896-98, 18 to 20.

on hydrolysis give the polymetaphosphimic. acids, which are ring compounds formed from phosphoric acid molecules, held together by imido-groups, *e.g.*:

Hexametaphosphimic acid:

$$HN \begin{array}{c} O \ OH \quad H \quad O \ OH \quad H \quad O \ OH \\ \nwarrow / \quad | \quad \nwarrow / \quad | \quad \nwarrow / \\ P \!-\!\!\!-\! N \!-\!\!\!-\! P \!-\!\!\!-\! N \!-\!\!\!-\! P \\ \qquad\qquad\qquad\qquad\qquad\qquad NH \\ P \!-\!\!\!-\! N \!-\!\!\!-\! P \!-\!\!\!-\! N \!-\!\!\!-\! P \\ / \searrow \quad | \quad / \searrow \quad | \quad / \searrow \\ HO \quad O \quad H \quad HO \quad O \quad H \quad HO \quad O \end{array}$$
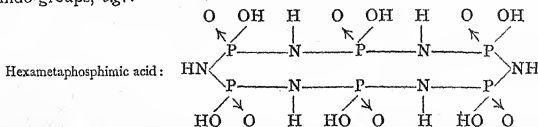
Their decomposition products, which form open chains, *e.g.* tri-imido-tetraphosphoric acid,

$$PO(OH)_2 . NH . PO(OH) . NH . PO(OH) . NH . PO(OH)_2,$$

may also be produced on hydrolysis.

Of the phosphorus chloronitrides, the following well-defined compounds are known, besides some which contain more than seven phosphorus atoms and which have not been isolated in the pure state.

		Melting Point.	Boiling Point at 13 mm.	Boiling Point at 760 mm.
$(PNCl_2)_3$	Tri-phosphor-chloronitride	114°	127°	265.2°
$(PNCl_2)_4$	Tetra- ,, ,,	123.5°	188°	328.5°
$(PNCl_2)_5$	Penta- ,, ,,	41°	223-24°	
$(PNCl_2)_6$	Hexa- ,, ,,	91°	261-63°	Polymerise
$(PNCl_2)_7$	Hepta- ,, ,,	>18°	289-94°	
$(PNCl_2)_x$	Poly- ,, ,,	< Red heat	Depolymerises	

Only the tri- and tetra-compounds are formed when PCl_5 and NH_4Cl are heated together at 150°-200°. They may conveniently be separated by fractional distillation. If, however, the mixture is heated for a longer time, particularly at about 350°, they polymerise to the higher products, and are finally converted into the poly-phosphor-chloronitride, which is remarkable for its exceptional properties. It forms an elastic mass which may be drawn out like rubber and cut with scissors. In the pure state it is colourless, transparent and insoluble in all neutral solvents. It absorbs benzene vapour in large quantities, when it swells to four times its volume and finally assumes a jelly-like consistency; on evaporating the benzene it is again completely converted to its initial condition. The adsorption of the benzene by the colloidal chloronitride is thus reversible. On heating the polymerised product to a high temperature depolymerisation sets in, giving a mixture of lower chloronitrides. An equilibrium is set up between the polymerised product and the lower molecular forms, like that obtained in the preparation of the polymerised product by heat. If the chlorine atoms are replaced by organic amine radicals, all the polymers give the same unimolecular substitution product.

Phosphorus chloronitrides are attacked by water with difficulty, probably because they are not wetted by it. On the addition of ether, they are wetted and therefore hydrolysed, giving metaphosphimic acids. The formulae of the chloronitrides are thus closely related to those of the phosphimic acids:

$$
\begin{array}{c}
\text{Cl}\quad\text{Cl} \\
\diagdown\diagup \\
\text{P} \\
\diagup\diagdown\diagdown \\
\text{N}\qquad\text{N} \\
\text{Cl}\diagdown\mid\qquad\mid\diagup\text{Cl} \\
\quad\text{P}\diagdown\quad\diagup\text{P} \\
\text{Cl}\diagup\quad\text{N}\quad\diagdown\text{Cl}
\end{array}
\qquad
\begin{array}{c}
\text{Cl}_2\text{P}\!\!-\!\!\text{N}\!\!=\!\!\text{PCl}_2 \\
\parallel\qquad\mid \\
\text{N}\qquad\text{N} \\
\mid\qquad\parallel \\
\text{Cl}_2\text{P}\!\!=\!\!\text{N}\!\!-\!\!\text{PCl}_2
\end{array}
\quad\text{etc.}
$$
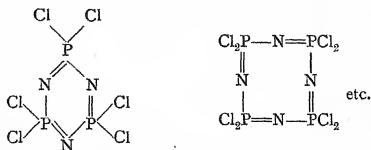
Hydrolysis is accompanied by rearrangement of the pentacovalency of phosphorus:

$$
\begin{array}{c}
\text{Cl}\quad\text{Cl} \\
\diagdown\diagup \\
\text{P} \\
\diagup\diagdown \\
\text{N} \\
\mid
\end{array}
\longrightarrow
\begin{array}{c}
\text{OH}\ \ \text{OH} \\
\diagdown\diagup \\
\text{P} \\
\diagup\diagdown \\
\text{N} \\
\mid
\end{array}
\longrightarrow
\begin{array}{c}
\text{O}\quad\text{OH} \\
\diagdown\diagup \\
\text{P} \\
\diagup\diagdown \\
\text{HN} \\
\mid
\end{array}
$$
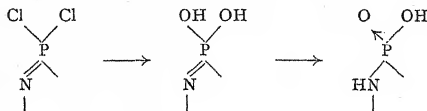
These ring structures, however, only exist as far as hexametaphosphimic acid (formula, p. 650), and more highly polymerised members form the open chains of the imide-polyphosphoric acids (cf. formulae, p. 652).

Tetrametaphosphimic acid is by far the most stable of the series; it may be heated for hours with acid without undergoing complete decomposition. In such circumstances trimetaphosphimic acid is broken down in a few minutes, and the di- and mono-acids cannot be prepared at all.

Only the tri- and tetra-metaphosphimic acids form characteristic salts. The higher members of the series give completely amorphous or syrupy metallic compounds. The normal salts, in which all the H atoms of the OH groups are replaced by metal, tend to hydrolyse, and therefore give an alkaline reaction, which becomes more pronounced in the more highly polymerised molecules. Here again the silver salts are particularly characteristic; they are sparingly soluble and white, as long as their silver content is no greater than that of hydroxyl groups. But additional silver atoms may be introduced, and these compounds, in which silver replaces the imide hydrogen, are coloured yellow to orange, like all silver-nitrogen compounds.

On boiling with acids the rings are split owing to hydrolysis,

with the elimination of ammonia, and the remaining portions of the ring form open chains, *e.g.* :

Trimetaphosphimic acid.   Di-imido-triphosphoric acid.
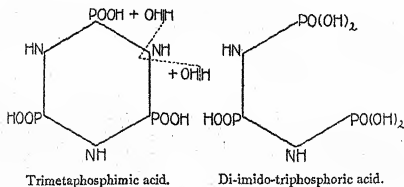
Smaller fragments may also be formed occasionally, *e.g.* imidodiphosphoric acid, $(OH)_2 . PO—NH—PO . (OH)_2$ from trimetaphosphimic acid. On the other hand, however, hydrolysis may proceed incompletely, so that NH is not split out in the rupture of the ring, but an amido-phosphoric acid is formed by the addition of a water molecule :
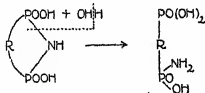
These compounds, which exist in considerable numbers, are sometimes only known in the form of their salts and have very characteristic silver salts. The end member of the series is the substance phosphimideamide. This is certainly polymerised and has the formula

$$\left(\begin{array}{c} PO \diagup NH \\ \diagdown NH_2 \end{array}\right)_x$$
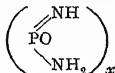
It is formed by the action of ammonia and water on phosphorus pentachloride.

Phosphoric acid also gives amide compounds of the hydrazide form, for example, the salts of hydrazidophosphoric acid :

$$NH_2 . NH . PO_3H_2.$$
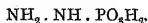
On the other hand, as in sulphuric acid, compounds of phosphoric acid which contain a PH_2 or AsH_2 radical instead of an OH or NH_2 group are not known.

Hydrazine and Hydroxylamine

Hydrazine, $H_2N . NH_2$, and hydroxylamine, NH_2OH, are derived from ammonia by the substitution of a hydrogen atom by an NH_2 or OH group respectively. Like ammonia, both enter into co-ordination compounds. Their complexes with hydrogen thus form positive radicals like ammonium (*cf.* p. 615), and form hydrazinium and hydroxylaminium salts corresponding to ammonium salts. Aqueous solutions of N_2H_4 and NH_2OH similarly react as bases.

They also resemble NH_3 in their property of giving off hydrogen

(*cf.* p. 606), but actually decompose much more readily. Since their heat of formation is negative at low temperatures, their tendency to decompose is greater; the decomposition is not reversible like that of ammonia, and may occur with explosive violence. In NH_2OH there is also the possibility of intramolecular transposition, since the NH_2 group may have a reducing effect on the OH group. A powerful reducing action is characteristic of both compounds.

Again, as in ammonia, the hydrogen may be replaced by metals. The general instability of the metallic amides increases, in these metallic derivatives, to the point of explosiveness.

Preparation.—*Hydrazine* is best prepared by double decomposition between chloramine and excess of ammonia :

$$NH_2 . \overline{H + Cl} . NH_2 \xrightarrow{-HCl} NH_2 . NH_2.$$
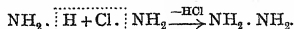
Chloramine is first prepared by the interaction of sodium hypochlorite and ammonia :

$$NH_2 . \overline{H + OH} . Cl \xrightarrow{-H_2O} NH_2Cl.$$
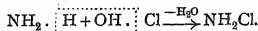
The formation of hydrazine, however, only takes place smoothly if a small quantity of glue is added to the solution, otherwise the chloramine decomposes into nitrogen, hydrochloric acid and ammonia. The effect of the glue appears to depend on its action in raising the viscosity, and it may be replaced by other substances which have a similar effect.[1] The ammonia appears to be adsorbed on the glue particles ; no compound of glue and chloramine is formed,[2] nor does the glue increase the stability of the chloramine.[3] The hydrazine is isolated in the form of its sulphate, which is very sparingly soluble—at 22°, 1 part dissolves in 33·parts of water, but the solubility increases rapidly with rising temperature.

Hydrazine is also found when ammonia is subjected to bombardment by electrons, but only in 0·5 per cent. yield (König).

All other methods of preparing hydrazine have only a theoretical interest. Two main types of reaction can be used. In one, oxidised hydrazines are reduced and the radical attached to hydrazine is finally split off.

To this type belongs the reduction of nitramide, $NH_2 . NO_2$, with amalgam, which can be carried out by using substituted nitramides, *cf.* p. 639. The whole process of the reaction is as follows [4] :

$$HN : C \underset{NH_2}{\overset{NH . \overline{H + OH} . NO_2}{\diagup}} \xrightarrow{-H_2O} HN : C \underset{NH_2}{\overset{NH . NO_2}{\diagup}} \xrightarrow[\text{with H}]{\text{redn.}} HN : C \underset{NH_2}{\overset{\overset{HO . H}{NH . NH_2}}{\diagup}} \longrightarrow$$

Guanidine.   Nitroguanidine.   Amidoguanidine.

$$\underset{\text{Urea.}}{H_2N - \overset{\overset{O}{\|}}{C} - NH_2} + \underset{\text{Hydrazine.}}{H_2N . NH_2}$$
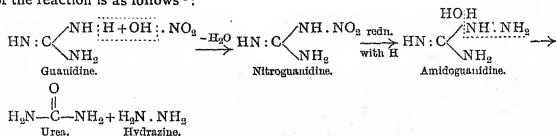
[1] Raschig, *Chem. Zeit.*, 1907, 926.   [2] Joyner, *J. Chem. Soc.*, 1923, 123, 1114.
[3] Raschig, *Schwefel- u. Stickstoffstudien*, p. 67.   [4] Thiele, *Ann.*, 1892, 270, 31.

Potassium nitrososulphite, $K_2SO_3 . 2NO$, also gives large quantities of hydrazine when reduced with sodium amalgam (cf. p. 646). Hyponitrous acid, on reduction with hydrogen sulphide in ammoniacal solution, also yields hydrazine:

$$HO.N:N.OH \xrightarrow{H_2S} H_2N.NH_2.$$
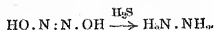
The other method depends on the hydrolysis of aliphatic diazo- or hydrazo-compounds, i.e. compounds containing the radicals

$$N_2:C\Big\langle \qquad \text{or} \qquad N_2H_2:C\Big\langle$$
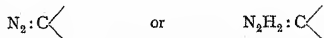
The hydrolysis proceeds most simply when the esters of bisdiazo-acetic acid are treated with dilute sulphuric acid, giving hydrazine and oxalic acid[1]:

$$\begin{matrix} H_2 & O \\ (N_2 = CH.CO_2H)_2 \\ H_2 & O \end{matrix} \rightarrow N_2H_4 + CO_2H.CO_2H.$$
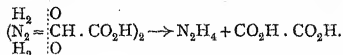
On the other hand, non-polymerised diazoacetic esters must first be reduced, in order that hydrazine and glyoxalic acid may be obtained from them:

$$\underset{\text{Diazoacetic acid.}}{N_2:CH.CO_2H} \xrightarrow{+H_2} \underset{\text{Hydrazoacetic acid.}}{N_2H_2:CH.CO_2H} \xrightarrow{H_2 \ \ O} \underset{\text{Glyoxalic acid.}}{N_2H_4 + CHO.CO_2H}$$

The preparation from an addition compound of potassium cyanide and bisulphite, an acid potassium salt of the acid $NH_2.CH:(SO_3H)_2$, is very successful. This is first converted into the diazo-compound by nitrous acid:

$$N\Big\langle\begin{matrix} O & H_2 & N \\ + & & | \\ OH & H & C = (SO_3H)_2 \end{matrix} \xrightarrow{-2H_2O} N_2:C:(SO_3H)_2;$$
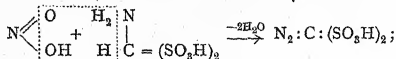
sulphite is added to this, and the addition product hydrolysed:

$$\begin{matrix} O & H_2 + H & O & H \\ H_2SO_3 \ \dots\dots N_2 & :C: & (SO_3H)_2 \\ H & O & H \end{matrix} \longrightarrow H_2SO_4 + N_2H_4 + CO_2 + 2H_2SO_3.$$
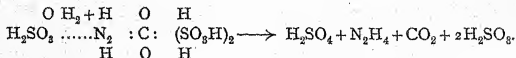
Hydroxylamine is prepared by simpler methods. The hydrolysis of hydroxylamine monosulphonic acid,

$$HO.NH.\underline{SO_3H + HO}.H \xrightarrow{-H_2SO_4} HO.NH_2,$$
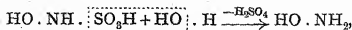
has already been described on p. 641. Sulphite and nitrite are regenerated if the hydrolysis is carried out in alkaline solution. All other methods depend on the reduction of more highly oxidised nitrogen compounds. With the exception of nitrous oxide, all the oxides and acids of nitrogen which contain oxygen may be reduced to

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[1] Curtius and Jay, *J. prakt. Chem.*, 1889, 39, 27.

hydroxylamine, but the yield is generally low when chemical reducing agents are employed, since other reduction products preponderate. But gaseous nitric oxide yields noticeable quantities of hydroxylamine if it is passed into a hot mixture of tin and hydrochloric acid (nascent H). Nitrites and nitrates behave similarly, and on reduction with amalgam, sulphuretted hydrogen, hydrosulphurous acid, etc., in alkaline solution, always give hydroxylamine as well as other reduction products. Ethyl nitrate, $C_2H_5NO_3$, may be used with advantage as a nitrogen derivative for reduction.[1] These methods do not serve for the preparation of large quantities, but an excellent yield of hydroxylamine is obtained by the electrolytic reduction of nitrites or free nitric acid,[2] which is converted almost exclusively into hydroxylamine and ammonia. The relative proportions of these two products depend entirely on the nature of the metal used for the cathode. Cathodes of pure mercury or amalgamated electrodes of other metals give mainly hydroxylamine. With lead cathodes, on the other hand, the portion of the nitric acid converted into hydroxylamine amounts at the most to 40 per cent., on electrodes of bright copper 15 per cent., and on those of spongy copper it diminishes to 1 per cent., so that here almost all the nitric acid is converted to ammonia. This phenomenon is probably not due to the further reduction of the hydroxylamine to ammonia at such electrodes; for this takes place very slowly (Tafel).

Preparation of Anhydrous Hydrazine and Hydroxylamine.—The preparation of the anhydrous compounds is difficult as they decompose easily. Hydroxylamine is very unstable and cannot be separated from its aqueous solution by fractional distillation as it is very volatile in steam. Methyl alcohol solutions are therefore used, which can be obtained by decomposing hydroxylaminium chloride with sodium methoxide:

$$NH_2OH \cdot HCl + CH_3ONa \longrightarrow NH_2OH + CH_3OH + NaCl.$$
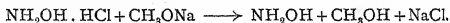
A simple method of preparing hydroxylamine without danger or distillation, by freezing out such methyl alcohol solutions, has been worked out.[3]

It may also be obtained from solid anhydrous hydroxylamine compounds, by heating under reduced pressure; the tertiary phosphate, in particular, yields it at moderate temperatures. Addition compounds of hydroxylamine also decompose. Thus hydroxylamine distils off from $ZnCl_2 \cdot 2NH_2OH$ on warming *in vacuo*; this complex is formed by dissolving zinc oxide in hydroxylamine hydrochloride.

Anhydrous hydrazine may be prepared pure with little trouble. The simple distillation of the aqueous solution, obtained by decomposing

[1] Lossen, *J. prakt. Chem.*, 1865, 96, 462.

[2] Tafel, *Z. anorg. Chem.*, 1902, 31, 289.

[3] Lecher and Hofmann, *Ber.*, 1922, 55, 1912.

the sulphate with barium hydroxide, is not successful, as an addition compound of hydrazine with one molecule of water, hydrazine hydrate, N_2H_4, H_2O, is formed, a strongly refracting liquid with a faint odour, b.pt. 118·5°. This hydrate, as shown by vapour density estimations, is only completely split up into hydrazine and water at 138°, but if it is heated in the presence of solid potassium hydroxide, the latter takes up the water completely and anhydrous hydrazine distils.

Properties. — The free compounds have the following physical properties:

	Melting Point.	Boiling Point.	Density.
N_2H_4	1·8°	113·5° (760 mm.)	1·0
NH_2OH	33°	57° (22 mm.)	1·35

They are very hygroscopic and hydrazine fumes copiously in damp air; they mix with water and the lower alcohols in all proportions; hydroxylamine is sparingly soluble in the higher alcohols. They dissolve only sparingly in other organic solvents, their solubility relationships being similar to those of water. Many salts dissolve in them just as they do in liquid ammonia. Hydroxylamine has no odour, hydrazine hardly any. In the pure condition they can be kept either in the anhydrous state or in aqueous solution; they decompose, however, in the presence of small quantities of alkali. The decomposition may take place in various ways, and the actual reaction depends on the nature of the added catalyst.[1] Thus, in alkaline solution, hydroxylamine decomposes into ammonia, nitrogen and water, but in the presence of some platinum black, nitric oxide is formed instead of nitrogen. Hydrazine yields ammonia, nitrogen and water on decomposition under all conditions, but the proportions differ. In neutral solution the reaction is catalysed by platinum, according to the equation $2N_2H_4 \longrightarrow 2NH_3 + N_2 + H_2$, but in the presence of a little alkali, $3N_2H_4 \longrightarrow 2NH_3 + 2N_2 + 3H_2$.

As a result of the endothermic nature of these compounds and the large quantities of gas formed when they decompose, their dissociation may lead to violent explosions. For example, when a single drop of hydroxylamine is heated in a test-tube over a free flame, it decomposes with a noise like a gun going off. Explosions are also observed in the preparation of hydrazine, but they can be avoided by careful work. Hydrazine may be heated to about 350° in the pure condition without decomposition. Smaller quantities of both substances burn quietly in the air, hydroxylamine with a violet, and hydrazine with a yellow flame.

Anhydrous hydrazine yields colloidal solutions of elements very readily; this tendency has already been noted in liquid ammonia, but here it is still more strongly developed. Thus sodium dissolves in

[1] Tanatar, *Z. physikal. Chem.*, 1902, 40, 475; 41, 37.

hydrazine with a deep blue colour, sulphur with a brown, green or blue colour, selenium gives a red colloidal solution, stable even after dilution with water, yellow phosphorus a deep blackish-brown liquid, and even metallic arsenic in hydrazine gives a coloured solution, from which a red-brown, non-metallic, flocculent precipitate is deposited. If such colloidal solutions, *e.g.* that of sulphur, are not rapidly diluted with water, the reducing action of hydrazine becomes apparent, and the double decomposition $N_2H_4 + 2S \longrightarrow N_2 + 2H_2S$ takes place, just as hydrazine may be completely oxidised to nitrogen and water, $N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$ by the oxygen of the air.

This reducing action is very characteristic of hydrazine and hydroxylamine. Strong oxidising agents like potassium permanganate are reduced explosively on being added to those two substances in concentrated form; weaker and more dilute solutions undergo reduction according to simple equations, so that these reactions find many different applications in analytical chemistry. Indeed, a complete analytical process for the qualitative detection of the elements may be built up successfully by making use of the reducing power of these reagents (Ebler). Their reaction with the salts of the more noble metals is especially characteristic. These are easily reduced to the metal (Ag, Au and Hg salts), or yield less oxidised substances (Fehling's solution). This reducing effect seldom appears except in alkaline solution. Ferric salts are reduced by hydroxylamine in acid solution, $4FeCl_3 + 2NH_2OH \longrightarrow 4FeCl_2 + N_2O + 4HCl + H_2O$, but ferrous hydroxide, suspended in dilute caustic soda, is oxidised to ferric hydroxide, $2Fe(OH)_2 + NH_2OH + H_2O \longrightarrow 2Fe(OH)_3 + NH_3$. Measurements of their reduction potentials show that such alkaline solutions are very strong reducing agents (*cf.* p. 164).

The difference in reactivity of the alkaline and acid solutions probably depends on the formation of salts of hydroxylamine and hydrazine, in which the amido-hydrogen is replaced by metal. These salts have a great tendency to decompose. Sodium hydrazide, $NH_2 . NHNa$, corresponding to sodamide, $NaNH_2$, is obtained by dissolving metallic sodium in liquid hydrazine. From the deep blue solution which is first formed, the white hydrazide is formed later with the evolution of hydrogen. This is a most dangerous compound on account of its instability; a breath of air or contact with moisture is sufficient to cause a powerful detonation.[1] Hydroxylamine also gives similar explosive compounds, but here the OH hydrogen is first replaced by metal, and compounds like $NH_2 . ONa$ are much less dangerous.

Hydroxylamine and hydrazine, like water and ammonia, co-ordinate with salts as neutral components. Thus the chlorides of most tervalent metals add on two molecules of NH_2OH or of N_2H_4. The compounds of mercury and of platinum are interesting, as they are formed only

[1] Schlenk and Weichselfelder, *Ber.,* 1915, 48, 669.

in non-aqueous solvents, being immediately reduced to the metal in the presence of water. These compounds are completely analogous to the amines, but the tendency for addition to occur is less; but in certain circumstances six molecules of the neutral component may enter, as with ammonia. Thus, a compound $[Ni(NH_2 . OH)_6]SO_4$ is known, which is red, and in some compounds, corresponding to the cobaltammines and chromammines, e.g.:

$$\left[Co(NH_2 . OH)_6\right]X_3 \qquad \left[Pt(N_2H_4)_4\right]X_2 \qquad \left[Pt\substack{(NH_3)_2 \\ (N_2H_4)_2}\right]X_2 \text{ (cis andtrans),}$$
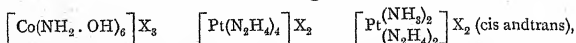
the linking of the hydroxylamine or hydrazine is not markedly less stable than that of ammonia. The hydroxylamine may be driven off from them by heating.

The most important addition products of this kind are, however, the hydrazinium and the hydroxylaminium salts, which correspond in many respects to the ammonium salts:

$$\left[NH_4\right]Cl \qquad \left[N\substack{H_3 \\ OH}\right]Cl \qquad \left[N\substack{H_3 \\ (NH_2)}\right]Cl$$

Ammonium chloride.   Hydroxylaminium chloride.   Hydrazinium chloride.
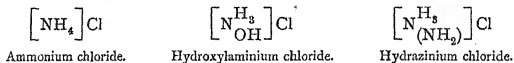
Hydrazine, which contains two NH_2 groups, can also utilise the second one in forming addition compounds, e.g. $Cl[H_3N\{N\}H_3]Cl$. It thus forms two series of salts, in which it is attached either to one or to two hydrogen atoms:

"Monobasic" salts   . N_2H_4, HCl N_2H_4, HNO_3 $2N_2H_4$, H_2SO_4
"Dibasic" salts   . N_2H_4, 2HCl N_2H_4, $2HNO_3$ N_2H_4, H_2SO_4
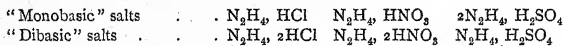
Since the affinity of N_2H_4 and NH_3OH for the H atom is weaker than that of ammonia, the decomposition of the hydrazinium and hydroxylaminium salts in aqueous solution is more complete than that of the ammonium salts. The salts of hydroxylamine therefore have a definitely acid reaction, and the aqueous solution of the base is less alkaline than ammonia, as it contains only a few $[H . NH_2OH]OH$ molecules, and therefore less OH' ions than are present in aqueous ammonia. The compounds of hydrazine with two acid radicals also lose one of them easily. This decomposition is partial in aqueous solution, and N_2H_4. 2HCl, on dry heating to about 140°, loses one molecule of HCl and is converted into N_2H_4. HCl.

On the other hand, more than one NH_2OH molecule may be added to the hydrogen atom of acids as a neutral component. Compounds such as $[H(NH_2OH)_2]Cl$, $[H(NH_2OH)_2]Br$, $[H(NH_2OH)_2]I$, and even $[H(NH_2OH)_3]I$ are known, which are even slightly more stable than the corresponding ammonia compounds (p. 617). More than one molecule of hydrazine may also be added on to HI.

Most salts of hydrazine and hydroxylamine are very easily soluble in water; many are even somewhat deliquescent. Only the oxalate

ana the tertiary phosphate of hydroxylamine are sparingly soluble, and both, at room temperature, dissolve to about 1·5 parts per 100 of water. Hydroxylamine hydrochloride is somewhat soluble in hot ethyl alcohol, and may be separated in that way from admixed alkali chlorides.

Nitrohydroxylamine is formed as its sodium salt when a solution of the sodium derivative of hydroxylamine is decomposed with ethyl nitrate:

$$HO.NH\underbrace{H+C_2H_5.O}.NO_2 \xrightarrow{-C_2H_5OH} HO.NH.NO_2$$

or

$$NH_2.O\underbrace{H+C_2H_5.O}.NO_2 \xrightarrow{-C_2H_5OH} NH_2.O.NO_2.$$
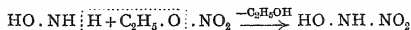
It is uncertain whether either of these constitutional formulae give the structure of this acid, which is known only in the form of its salts. It seems more likely that there is a relationship between the atoms which cannot be expressed by main valencies, since the compound easily breaks up (*e.g.* on acidification) into 2NO and H_2O. Thus NO groups must exist in it. The formation of yellow silver salts shows that it contains hydrogen, adjacent to nitrogen, which is replaceable by metals. The relationship between the two nitrogen atoms is shown by the formation of N_2O on boiling, and on fusion NaON : NONa is formed, and then nitrite.[1] There obviously exists a relationship between all the atoms which is strengthened in certain directions and loosened in others with alteration in conditions.

Dihydroxylamine, $NH(OH)_2$.—Tafel[2] regards this compound as an intermediate product in the electrolytic reduction of nitric acid to ammonia. It cannot be isolated any more than can *di-imide*, $HN : NH$, or longer nitrogen chains such as $NH_2.NH.NH_2$, organic substitution products of which are well known. Instead of the simple nitrogen compounds, nitrogen, ammonia and hydrogen always appear. On the other hand, a structure in which three nitrogen atoms are in contact with each other without being burdened with organic residues appears in hydrazoic acid.

Hydrazoic Acid, Azoimide, N_3H

Structure.—The cyclic formula $H—N\left\langle\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix}\right.$ was accepted for this very explosive substance until Thiele[3] brought forward evidence for the straight chain structure $H—N=N\equiv N$. The cyclic formula is possible electronically but if Thiele's formulation is accepted the octet must be abandoned for nitrogen. The modified structures $H—N=N\rightarrow N$ and $H—N\leftarrow N\equiv N$, however, retain octets.

The examination of sodium and potassium azide crystals by means of X-rays[4] shows a linear arrangement of the three nitrogen atoms

[1] Angeli and Angelico, *Gazzetta*, 1900, **30**, I, 593.
[2] *Z. anorg. Chem.*, 1902, **31**, 293.   [3] *Ber.*, 1911, **44**, 2522.
[4] Hendricks and Pauling, *J. Amer. Chem. Soc.*, 1925, **47**, 2904.

in the N_3' ion, and further discloses the fact that this ion has a centre of symmetry; it may, therefore, be written $N \rightleftharpoons N \longrightarrow N$ (*i.e.* $\overset{4}{N} \equiv N \equiv \overset{4}{N}$). The structure of potassium cyanate, containing the ion $\overset{4}{N} \equiv C \equiv \overset{4}{O}$, is almost identical.

The ion is easily converted to the covalently linked form, *e.g.* in the organic azides, and the results of Lindemann and Thiele[1] based on parachor measurements, and also those of Sidgwick[2] based on a comparison of boiling points, were in favour of the cyclic formula, but the evidence was not conclusive. Brockway and Pauling,[3] however, determined the structure of methylazide by the electron diffraction method. They found the azido group to be linear and the distances between the atoms in Ångstrom units to be

$$N \ 1\cdot26N \ 1\cdot10N.$$
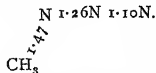
The linear arrangement is also established by X-ray analysis of cyanuric triazide[4] which has the structure:

i.e.
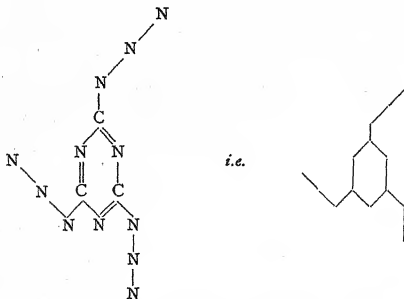
The arrangement of the bondings in the linear azido group is not considered in this formulation.

Each of the formulae $-N=N \rightarrow N$ and $-N \leftarrow N \equiv N$ should possess a considerable dipole moment, owing to the presence of the co-ordinate link; the moment of azides is, however, quite small.[5] This small moment, and also the interatomic distances and the heat of

[1] *Ber.*, 1928, 61, 1529.   [2] *J. Chem. Soc.*, 1929, 1108.
[3] *Proc. Nat. Acad. Sci.*, 1933, 19, 860.
[4] Knaggs, *Proc. Roy. Soc.*, 1935, A150, 576; Hughes, *J. Chem. Physics*, 1935, 3, 1.
[5] Bergmann and Schütz, *Nature*, 1931, 128, 1077; Sidgwick, Sutton and Thomas, *J. Chem. Soc.*, 1933, 408.

formation of the azido grouping[1] can only be accounted for by assuming that the azido grouping is a resonance-hybrid of these two forms.[2] Hydrazoic acid likewise is, therefore, a hybrid between $H—N \leftarrow N \equiv N$ and $H—N = N \rightleftharpoons N$; the dipoles in these two extremes operate in opposite directions, and the hybrid should, therefore, show only a small moment.

Many syntheses of hydrazoic acid and its salts, the azides, depend on treating hydrazine, or one of its derivatives, with a substance containing nitrogen, which withdraws hydrogen and adds nitrogen. For this, either nitrogen trichloride, or better, nitrous acid, is used:

$$N_2H_4 + NCl_3 \longrightarrow N_3H + 3HCl,$$
$$N_2H_4 + HNO_2 \longrightarrow N_3H + 2H_2O.$$
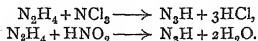
The ethyl ester of nitrous acid is more conveniently employed for this preparation. It reacts similarly in alkaline and in acid solution, but in neutral solution hydrazine nitrite, $N_2H_4 . HNO_2$, decomposes quite differently, viz. into ammonia, nitrous oxide and water.

Free hydrazine was formerly very difficult to obtain, so various substituted hydrazines were used to carry out this synthesis by means of nitrite, and the substituents subsequently removed. Thus amidoguanidine (cf. p. 653) with nitrous acid yields diazoguanidine, which, in the presence of alkali, gives hydrazoic acid by loss of water and hydrolysis:
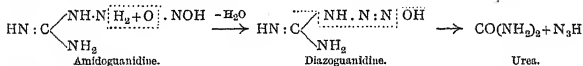
The products formed when hydrazine is oxidised, e.g. with persulphates, may yield azoimide. Hydrazoic acid is formed, in particular, from mixtures of hydrazine and hydroxylamine on oxidation with H_2O_2 or $K_2Cr_2O_7$.

The best method of preparing the salts of hydrazoic acid makes use of nitrous oxide as the source of the combined nitrogen. This gas, passed into molten sodamide, condenses smoothly with it:

$$NaN \vdots H_2 + O \vdots N_2 \xrightarrow{-H_2O} NaN_3,$$
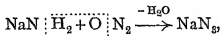
which is accompanied by the hydrolysis of a further molecule of sodamide by the water which is simultaneously formed. It is interesting to note, though it is not of practical importance, that alkali azides may be directly synthesised from the metals and nitrogen by reaction under the influence of the electric discharge.[3] With lithium small quantities of nitride only are formed, but with K, Cs and Rb, azides are formed, accompanied by small quantities of nitrides as secondary products.

[1] Roth and Müller, Ber., 1929, 62, 1190.
[2] Sidgwick, Trans. Faraday Soc., 1934, 30, 801.
[3] Moldenhauer, Ber., 1929, 62, 1954.

Potassium azide may also be obtained by warming potassium nitrate and potassamide in liquid ammonia:

$$KNO_3 + 3KNH_2 \longrightarrow KN_3 + 3KOH + NH_3.$$
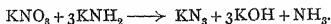
Free hydrazoic acid is obtained without difficulty from its salts by distillation of their aqueous solutions acidified with sparingly volatile acids, or directly from the solid potassium salt and concentrated sulphuric acid. Since hydrazoic acid has a low boiling point ($37°$) it passes over before the water, and even when obtained from dilute solutions it contains only a small percentage of water, which can be removed by drying with calcium chloride. The water-white mobile liquid solidifies at $-80°$, and has an unbearably pungent smell, which, on account of the volatility of the acid, is apparent even in dilute solutions, and may be compared with that of hydrofluoric acid, though it acts even more strongly on the mucous membrane. The acid is unimolecular in the state of vapour. It is equal to acetic acid in strength and hence its salts with weaker metals (Al) cannot be obtained from aqueous solution owing to hydrolysis, while those of the bases of medium strength can be obtained only in the basic form. On the other hand, salts of the alkalis, alkaline earths, lead and the univalent heavy metals are well known and resemble the halogen salts in many respects. Thus the salts of Pb, Ag, Hg^I, Cu^I, Tl^I, are almost insoluble in water, and so can be used to isolate the acid from dilute solutions. The deep red coloration which ferric salts give with hydrazoic acid is characteristic, and similar to that produced with thiocyanic acid, though it is formed at greater dilutions. Ferrous azide is converted to ferric azide if it is heated with excess of hydrazoic acid. If a solution of ammonium azide in liquid ammonia is electrolysed with anodes of a heavy metal, it is possible to obtain the azide of the metal. The ammonium and hydrazonium salts, NH_4N_3 and $N_2H_5N_3$ may be regarded as polymers of imide $(NH)_x$.

Hydrazoic acid has a strongly negative heat of formation:

$$3N + H + aq. = N_3H, aq. - 62 \cdot 1 \text{ Cal.}$$

It therefore decomposes with great violence and explosive force, since all the decomposition products are gaseous. The disruption is, however, subject to retardation, and the acid may be kept in aqueous solution almost as long as desired without any decomposition; in the presence of platinum black the acid breaks up with formation of ammonia. In the anhydrous condition it may also be kept in the cold if protected from shock; it explodes only on shaking or heating. Its salts show the explosive property to a very variable extent: while those of the univalent heavy metals are extremely explosive, others are susceptible only to strong percussion. Lead azide is used as a detonator in the explosives industry. Such salts can also withstand moderate heating. Others

again, especially the alkali salts, do not explode even on percussion, and may almost be melted without decomposition, as they explode only at high temperatures. The decomposition may be so arranged that it takes place gradually and gives a method for preparing pure nitrogen or pure metal, since decomposition into nitrogen and metal takes place unless a nitride is formed. The azide is used for the preparation of metallic radium.[1] A similar evolution of nitrogen is observed in the azides of

	Na	K	Rb	Cs	Ca	Sr	Ba
At about	280°	360°	310°	350°	100°	110°	120°.

The initial decomposition temperatures are often 50°-60° higher, but the reaction proceeds at a lower temperature when once started.[2]

Reducing agents first convert hydrazoic acid into hydrazine, and then quantitatively into nitrogen and ammonia: $N_3H + 2HI \longrightarrow N_2 + NH_3 + 2I$. The acid (in the presence of some thiosulphate) may easily be broken down to nitrogen by iodine: $2N_3H + I_2 \longrightarrow 3N_2 + 2HI$. But iodine acts quite differently on silver azide: here the silver is replaced by iodine, and *iodine azide* is formed: $N_3Ag + I_2 \longrightarrow N_3I + AgI$. This compound is not like nitrogen tri-iodide, except that it is even more explosive. It is white or slightly yellowish, and its sharp smell recalls that of iodine cyanide. There is, indeed, a general resemblance between the N_3 radical and the CN, CNS and halogen radicals. Iodine azide is quite soluble in water and many organic solvents, especially in ether, and in aqueous solution undergoes hydrolysis: $N_3I + H_2O \longrightarrow N_3H + IOH$, which takes place instantaneously in the presence of bases, so that iodine azide can be reconverted into potassium azide. On slow decomposition in non-aqueous solution, or in the solid state, iodine azide decomposes simply into nitrogen and iodine.[3] Bromine azide, N_3Br, has also been prepared.

Chlorazide, N_3Cl, is exactly analogous to iodine azide in its behaviour. It hydrolyses in aqueous solution in the presence of alkali, giving an azide and HOCl, but in acid solution the reaction is reversed:

$$N_3H + HOCl \underset{\text{Alkali.}}{\overset{\text{Acid.}}{\rightleftarrows}} N_3Cl + H_2O.$$
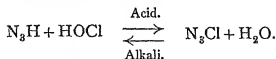
It may therefore be prepared by acidifying mixed solutions of sodium azide and hypochlorite with weak acids—even boric acid. If a drop of the mixed aqueous solutions of azide and hypochlorite is placed on scales of boric acid, the latter soon swell and become frothy, since chlorine azide is gaseous. It is colourless and has a similar odour to hypochlorous acid. Its explosive power is terrific, even in the gaseous state, and decomposition sometimes occurs without the

[1] Ebler, *Ber.*, 1910, 43, 2613.   [2] Tiede, *Ber.*, 1916, 49, 1742.
[3] Hantzsch, *Ber.*, 1900, 33, 522.

application of external force, when the containing vessel is shattered with the simultaneous appearance of pale blue flames.[1]

Sulphuryl azide, $N_3 . SO_2 . N_3$ is closely connected with the above compounds and is formed by the interaction of sulphuryl chloride and sodium azide.[2] It is a liquid soluble in benzene and not very explosive, so that it can be warmed in considerable quantities without great danger.

Azidodithiocarbonic Acid, $HS . CS . N_3$.—The addition of hydrazoic acid and its salts to carbon disulphide takes place when the components are warmed together in the same way as with secondary amines [3] :

$$
\begin{array}{ccc}
\underset{\underset{S}{\diagdown}}{C{:}S} + \underset{\underset{H}{\cdot}}{\overset{N{:}(C_2H_5)_2}{\quad}} \longrightarrow \underset{\underset{SH}{\diagdown}}{C{:}S}\overset{\diagup N{:}(C_2H_5)_2}{\quad} & & \underset{\underset{S}{\diagdown}}{C{:}S} + \underset{\underset{H}{\cdot}}{\overset{N_3}{\quad}} \longrightarrow \underset{\underset{SH}{\diagdown}}{C{:}S}\overset{\diagup N_3}{\quad} \\
\text{Diethyldithiocarbamic} & & \text{Azidodithiocarbonic} \\
\text{acid.} & & \text{acid.}
\end{array}
$$
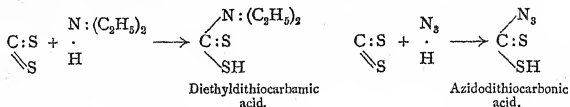
The salts of azidodithiocarbonic acid resemble those of xanthic acid and of substituted xanthic acids in many ways, especially in the formation of complex compounds. Thus the copper salt of diethyldithiocarbamic acid is so characteristic that it can be used as one of the most delicate tests for copper; azidodithiocarbonic acid also gives a fine yellow precipitate with cupric salts. In general, the heavy metal salts of the acid seem to be complex. Their explosive power varies; while the white, cheesy silver salt explodes at the slightest touch when dry, the alkali and alkaline earth salts containing water of crystallisation are considerably more stable. The free acid may also be obtained; with ferric salts it undergoes oxidation to a disulphide of enormous explosive power, of composition:

$$
\underset{\underset{S}{\parallel}}{N_3 . C} \text{—S—S—} \underset{\underset{S}{\parallel}}{C . N_3}.
$$
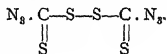
Lower Hydrides of Phosphorus

The formula,[4] but not the behaviour, of the liquid hydride of phosphorus, P_2H_4, corresponds to that of hydrazine. It is spontaneously inflammable in air and burns with a bright white flame. It is formed as a by-product in nearly all the preparations of PH_3; the P_2H_4 volatilises with the PH_3 and makes it spontaneously inflammable, even when only one part in five hundred is present. It can be separated as a colourless liquid by passing the mixture through a tube cooled in ice. This liquid boils at $52°$, the solid melts at $-99°$, and has a density about equal to that of water. P_2H_4 tends to decom-

[1] Raschig, *Ber.*, 1908, 41, 4194.   [2] K. F. Schmidt, *Ber.*, 1925, 58, 2411.
[3] Sommer, *Ber.*, 1915, 48, 1833.
[4] Royen and Hill, *Z. anorg. Chem.*, 1936, 229, 97.

pose into gaseous PH_3 and solid so-called $P_{12}H_6$. It is formed by the catalytic action of a little HCl gas on PH_3, and is thus obtained when PH_3 is passed into concentrated hydrochloric acid. The P_2H_4 in the spontaneously inflammable PH_3 may be removed by exposing the gas to light. Decomposition is also brought about by materials with large surface, e.g. charcoal and pumice. P_2H_4, in contrast to hydrazine, does not combine with acids. "Solid phosphorus hydride," $P_{12}H_6$, may be regarded as an elementary form of phosphorus of molecular size about P_{10}, which contains PH_3 in solid solution. The behaviour of the $P_{12}H_6$ agrees with this assumption; Royen[1] found that its composition varied from $P_{12}H_{4.5}$ to $P_{12}H_{6.4}$ and that a product $P_{12}H_{4.1}$ is produced by the interaction of phosphine and yellow phosphorus. There is no evidence for $P_{12}H_6$ or P_9H_2 from the X-ray diagrams, nor does the decomposition show a break at the P_9H_2 stage. The piperidine compound, formerly stated to be $P_{12}H_6pi_3$, is an adsorption complex of indefinite composition.

[1] *Naturwiss.*, 1936, 24, 108 ; *Z. anorg. Chem.*, 1936, 229, 369.

OXYGEN COMPOUNDS OF NITROGEN

Oxides of nitrogen—Nitrous oxide—Nitric oxide, nitrogen dioxide and trioxide—
Complex compounds of nitric oxide—Nitrosyl halogen compounds—Nitrogen
pentoxide — Nitric and nitrous acids - Nitrites — Nitrates — Hyponitrous acid
—Pernitric (Pernitrous) acid

Oxides.	Oxyacids.
Nitrous oxide, N_2O	Hyponitrous acid, $H_2N_2O_2$
Nitric oxide, NO	Hydronitrous acid, H_2NO_2
Nitrogen trioxide, N_2O_3	Nitrous acid, HNO_2
Nitrogen dioxide, NO_2	......
Nitrogen tetroxide, N_2O_4	......
Nitrogen pentoxide, N_2O_5	Nitric acid, HNO_3
Nitrogen peroxides $\begin{cases} NO_3 \\ N_2O_7 \end{cases}$	Pernitric acid, HNO_4 (?)
	Pernitrous acid $HO \cdot O \cdot NO$

The confusion which exists in the above nomenclature can be avoided by stating the numbers of each atom in the molecule, *e.g.* N_2O_3 is dinitrogen trioxide, NO_3 is nitrogen trioxide.

Of these compounds, the pairs $N_2O_3 : HNO_2$ and $N_2O_5 : HNO_3$ are related as anhydride and hydrate. N_2O, on the other hand, is not the anhydride of $H_2N_2O_2$. Nitrous and pernitric acids are known only in solution. Nitrous oxide occupies a special position among these compounds; while the others are easily interconvertible, nitrous oxide, although it may be obtained from the higher oxides, cannot be directly oxidised to them; its constitution is possibly very different from that of the others.

Nitrous Oxide, N_2O.—Nitrous oxide behaves like an addition compound of oxygen and nitrogen, N_2, O. The union between the two nitrogen atoms is closer than that of the oxygen to the nitrogen atoms; for its structure see p. 676.

Nitrous oxide is formed by the reduction of more highly oxidised nitrogen compounds, as well as by the elimination of water from one of the numerous compounds of the formula $N_2O \cdot xH_2O$, *e.g.* nitramide, NH_2NO_2; hyponitrous acid, $H_2N_2O_2$; hydroxylamine nitrite, NH_2OH, HNO_2, or ammonium nitrate, NH_4NO_3.

$$NH_2NO_2 \longrightarrow N_2O + H_2O \qquad NH_4NO_3 \longrightarrow N_2O + 2H_2O, \text{ etc.}$$
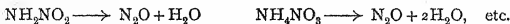
The last substance in particular is used as the raw material for its

preparation, since it is the cheapest of these compounds. On heating in the dry condition it yields fairly pure N_2O, with some NO as impurity. It is, however, unnecessary to use NH_4NO_3 itself; it is sufficient to use a mixture of sodium and potassium nitrates and ammonium sulphate, which yields nitrous oxide in just the same way at $170°$.

The preparation by mixing cold solutions of hydroxylamine hydrochloride and sodium nitrite proceeds readily, without heating.

If the oxygen content of the components yielding nitrous oxide is too small to combine with the whole of the nitrogen, a portion of the latter escapes as such, *e.g.* in the decomposition of hydrazoic acid with nitrous acid: $N_3H + HNO_2 \longrightarrow N_2 + N_2O + H_2O$; or ammonia is formed, *e.g.* in the decomposition of hydrazine nitrite in neutral solution: $N_2H_4, HNO_2 \longrightarrow N_2O + NH_3 + H_2O$.

In all these reactions the portion containing hydrogen acts as a reducing agent on the portion which contains oxygen. If, however, the hydrogen content is insufficient, nitrous oxide may be obtained from nitrogen compounds containing oxygen by the use of other reducing agents. Thus N_2O is prepared from nitric acid, nitrous acid or moist nitric oxide by means of all kinds of reducing agents, such as hydrogen sulphide, sulphurous acid, stannous chloride, sodium amalgam or metals and acids; $SnCl_2$ in particular is well adapted for this purpose. The N_2O is then less pure than when prepared according to the above methods; it contains much NO, which may be removed partially by washing with ferrous sulphate solution, or completely by washing with dichromate-sulphuric acid solution. Nitrous oxide may be obtained perfectly pure from its hydrate, $N_2O \cdot 6H_2O$, a solid which is stable at low temperatures but decomposes into its components below $0°$; or by the action of dilute acid on $K_2SO_4 \cdot N_2O$, which is formed[1] by the action of NO on sulphite solution.

Nitrous oxide is a colourless and almost odourless gas, which liquefies at $-89.5°$ and solidifies to colourless crystals at $-102.3°$. At $0°$ water dissolves almost its own volume, and alcohol four times its volume, of nitrous oxide; at $25°$ one volume of water dissolves about half a volume of the gas.

The heat of formation of nitrous oxide is -20 Cal. The tendency of the endothermic N_2O to decompose is shown by its powerful oxidising action, which, however, is not so vigorous as that of pure oxygen. The decomposition is subject to considerable retardation, and a powerful impulse, such as heat or a catalyst, is necessary to release it. For example, hydrogen can be heated with nitrous oxide to a fairly high temperature before explosion occurs, but in the presence of platinum sponge the reaction proceeds spontaneously, and the sponge glows. Phosphorus may be vaporised in N_2O, without reacting with it. Weakly burning sulphur is extinguished in it, but brightly burning sulphur, like ignited phosphorus, evolves sufficient heat to

[1] Gehlen, *Ber.*, 1931, 64B, 1267; 1932, 65B, 1130.

start decomposition and then burns briskly in the gas. Similarly, glowing charcoal burns in the gas, feebly glowing wood becomes inflamed, and heated metals, especially those whose oxides have a high heat of formation (cf. p. 441), burn readily. Nitrous oxide, like all other endothermic compounds, should become more stable at high temperatures, and the reaction $N_2O \rightleftharpoons N_2 + O$ then proceed perceptibly from right to left; but the conditions of experiment favourable to this synthesis have not yet been found, and thermo-chemical calculations show that even at temperatures above 1000° only vanishingly small yields are obtainable. Even the union of N_2O with more oxygen to form NO or N_2O has not been observed. In contrast to this, NO takes up oxygen rapidly to form NO_2. Unlike NO, nitrous oxide is quite stable to strong oxidising agents like $KMnO_4$ or Cl_2O. The most remarkable property of this gas is that of producing anæsthesia, for which purpose it is commonly applied in dentistry.

The Oxides of Nitrogen, NO, N_2O_3, $NO_2(N_2O_4)$—Preparation.— These oxides bear the closest chemical relationship to one another. Their modes of formation are completely identical in principle, and one oxide may be converted into another very readily. They are formed by the reduction of nitric acid; mixtures of two oxides are usually obtained. Further, NO_2 and N_2O_3 are formed by the oxidation of NO; the product formed depends only on the quantity of oxygen added. By thermal decomposition, NO_2 may be converted to NO and finally to N_2 and O_2, and by synthesis from nitrogen and oxygen, NO, N_2O_3 and NO_2 may be obtained.

Nitric acid may be reduced in numerous ways, but only a few give useful results. Among the reducing agents applied is arsenic trioxide, of which the glassy variety is mainly used, since the crystalline kind is too reactive owing to its high specific surface. The As_2O_3 gives one or other of the oxides of nitrogen according to the concentration of the acid, e.g.:

With HNO_3 of density	1·20	1·25	1·30	1·35	1·40	1·45
Products	almost pure NO	much NO little N_2O_3	little NO much N_2O_3	almost pure N_2O_3	1 part N_2O_3 1·3 „ NO_2	1 part N_2O_3 9 parts NO_2

Similarly, starch paste reduces nitric acid to varied products :

Density of acid .	1·33	1·40	Above 1·40
Product . . .	NO	some NO_2	much NO_2

NO_2 may be conveniently obtained by cautiously dropping formaldehyde, H . CHO, on to concentrated nitric acid.

Similar phenomena are observed in the reduction of nitric acid by such other reducing agents as free elements (metals as well as non-metals), salts of lower degrees of oxidation, sulphides, etc. The reduction of nitric acid by metals, sulphur, carbon, phosphorus, sulphides,

etc., when the acid used is very concentrated, proceeds only as far as NO$_2$. Further, the reaction goes to completion only in the presence of traces of NO$_2$; nitric acid which has been freshly prepared and is colourless hardly acts as an oxidant, even in the highest concentrations (Veley, 1890). If the nitric acid is diluted to sp. gr. 1·2 it oxidises the lower oxides of nitrogen very slowly; the acid can then be reduced by metals to nitric oxide NO, which is rendered impure by some N$_2$O. In particular, the metals which are below hydrogen in the electromotive series (p. 151) are available for the preparation of nitric oxide in this way, since if hydrogen were set free at the same time, further reduction of the NO would ensue. Copper is mainly used for this preparation, and goes into solution as copper nitrate. Mercury may also be used, but it is then desirable to dilute the nitric acid with sulphuric acid instead of water, as in the nitrometer.

If the reduction is carried out with excess of the reducing agent and in such a way that all the components of the reaction are in solution, a further reduction of the higher oxides which are initially formed can take place. This occurs in the reduction of dilute nitric acid by ferrous salts in solution; they are converted to ferric salts and reduce the nitric acid so completely to NO that the process may be used in the quantitative estimation of nitric acid; the NO may subsequently be easily driven out of the solution and its volume determined. Nitrites in acid solution act in the same way as nitrates.

The reduction of nitric acid may also be brought about by the action of heat. In this decomposition N$_2$O$_5$ may be considered the first member of the series; it is reduced to N$_2$O$_4$ on exposure to light at the ordinary temperature or on slight warming:

$$N_2O_5 \longrightarrow N_2O_4 + O.$$
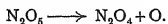
This splitting-off of oxygen is not reversible, and recombination does not take place at lower temperatures. Whenever N$_2$O$_5$ should be formed at higher temperatures, N$_2$O$_4$ or its depolymerisation product, NO$_2$, are formed. The acid is split up into its anhydride and water to a slight extent:

$$2HNO_3 \rightleftharpoons H_2O + N_2O_5,$$
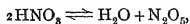
and as the equilibrium of this reaction lies mostly on the side of the undissociated acid, the decomposition of the acid soon ceases; but the small quantities of N$_2$O$_5$ which are contained in it gradually decompose as above and must be regenerated from the undecomposed acid, so that equilibrium is again restored. Both the dehydration of nitric acid and this secondary decomposition proceed more rapidly with rising temperature; the colourless nitric acid becomes reddish brown owing to the formation of NO$_2$. At a certain dilution, however, the decomposition practically comes to a standstill, owing to the excess of water on the right-hand side of the equilibrium.

Nitrates which do not give off oxygen to form nitrites on heating decompose into the metallic oxide and N_2O_5:

$$Pb(NO_3)_2 \longrightarrow PbO + N_2O_5,$$

but the N_2O_5 is not stable at the decomposition temperature, and it splits up into NO_2 and oxygen.

NO_2 can itself be decomposed by heat. It then forms NO and not N_2O_3, since the latter would be decomposed into NO and NO_2 at the temperature in question (cf. below). The decomposition of NO_2 differs from that of N_2O_5 in that it is reversible:

$$2NO_2 \rightleftharpoons 2NO + O_2.$$
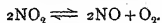
The decomposition is perceptible at about 150°, and is complete at 620°. Since it is accompanied by a change of volume its progress may be followed by the change in density of the gas. The decomposition at various temperatures is as follows:

Temperature	130°	184°	279°	494°	620°
Decomposition	0	5	13	56·5	100 %

At low temperatures, when the proper quantities are present, N_2O_3 is also formed by the combination of nitric oxide and oxygen; and in general it may be said that NO, O and NO_2 combine with each other with great ease, giving rise to various stages of oxidation within the limits NO—NO_2 dependent on the quantity of the individual substances present. There are thus the following possible reactions:

$$2NO + O \rightleftharpoons N_2O_3 \qquad\qquad NO + O \rightleftharpoons NO_2$$
$$NO + NO_2 \rightleftharpoons N_2O_3 \qquad 2N_2O_3 + 2O \rightleftharpoons 4NO_2.$$
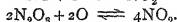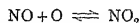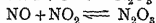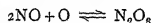
The preparation of the nitric oxide is the basic problem in the technical synthetic production of the oxides of nitrogen, and hence of nitric acid itself. This method of preparation of nitric oxide is difficult, as like all the oxides of nitrogen it is endothermic, nitrogen dioxide having the lowest heat of formation. They are only stable at ordinary temperatures owing to the retardation of their decomposition. In order to shift the equilibrium $2NO \rightleftharpoons N_2 + O_2$ to the left side to some extent, very high temperatures are necessary, but then the delay in decomposition is less, so that there is a danger of losing a considerable portion of the nitric oxide during the unavoidable cooling period. These relationships are made clear by the following numbers:

The establishment of the equilibrium is half finished at

Temp.	1000°	1500°	1900°	2100°	2900° T
	in 81·6 years	1·26 days	2·08 mins.	5·06 secs.	3·45 × 10⁻⁵ secs.

The percentage of nitric oxide in the equilibrium $N_2 + O_2 \rightleftharpoons 2NO$ is:

Temperature	.	1500°	2000°	2500°	2900°	3200°	4200° $T.$
Per cent. .	.	0·1	0·61	1·79	3·20	4·43	10

In order to obtain a fair yield an exceptionally high temperature must be employed; 4200° $T.$ corresponds approximately to that attained in the electric arc, and a favourable yield can then be obtained. At this temperature, however, not only the establishment of the equilibrium, but also the back decomposition, is very rapid, and it is necessary to bring the nitric oxide formed to a region of lower temperature as quickly as possible to avoid a great part of it being lost. This is carried out by having the arc suitably constructed, so that either it is spread out by an electro-magnet into a thin disc of flame, through which the N—O mixture (air) is blown, or the arc is kept in motion in the form of a sinuous, narrow, spiral band, or is forced into a water-cooled iron tube. In this way, on a laboratory scale, up to 8 per cent. of the mixture has been converted to nitric oxide, and in technical operations, up to 2·5 per cent. It is not only the thermal effect of the arc which is responsible for the formation of nitric oxide; under the influence of strong electric fields (silent discharges), oxygen and nitrogen are decomposed into atoms which can then combine to form nitric oxide. This process must also play a part in the arc process.

It may be mentioned that nitric oxide can also be obtained by passing electric sparks through liquid air, when very rapid cooling takes place. N_2O_3 is the chief product, and separates as a sky-blue powder.

Other sources of heat may be used in place of the arc for the formation of nitric oxide from its elements; the heat of explosion has been employed in this way. If hydrogen and oxygen are exploded in the presence of nitrogen, a temperature is reached which is sufficiently high to cause the nitrogen to combine with the oxygen. It is not necessary to use pure gases, but it is sufficient to explode a mixture of air and producer gas (Haeusser). In the ammonia equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$ there is a considerable quantity of free nitrogen present at 300°-500° (cf. p. 606). If the decomposition of the ammonia is favoured by the addition of a catalyst, the atomic nitrogen formed easily reacts with any oxygen present. In that way NO is formed, and if excess oxygen is present, it passes into NO_2. If the reaction temperature is too high, instead of nitric oxide being formed, the preponderating action is the formation of nitrogen molecules from the single atoms, and above 700° considerable quantities of molecular nitrogen are formed. The catalytic oxidation of ammonia to nitric oxide with platinum gauze or other catalysts now plays a prominent part in the industrial synthesis of nitric acid.

On the other hand, liquid NO decomposes under high pressures, though the reaction takes place so slowly at ordinary temperatures that a false equilibrium is established.[1] Very little nitrogen and no free oxygen are formed during the decomposition of the liquid; at 350 atm., for instance, the product contains: 1 per cent. N_2, 15 per cent. NO, 35 per cent. N_2O, and 49 per cent. N_2O_3.

N_2O_3 is the only one of these three oxides which is an acid anhydride, and it can therefore be obtained from the corresponding acid, nitrous acid, HNO_2, by elimination of water. Nitrous acid decomposes into N_2O_3 and H_2O spontaneously, in the same way that carbonic acid decomposes into CO_2 and H_2O. If a solution of a nitrite is acidified, N_2O_3 is immediately obtained. It is also formed in the hydrolysis of lead chamber crystals, when HNO_2 is the primary product:

$$NO(HSO_4) + HOH \longrightarrow HNO_2 + H_2SO_4.$$

Properties.—In the method of preparation last mentioned, N_2O_3 itself is not obtained if the reactions are carried out at room temperature, but only its decomposition products, NO_2 and NO. For, just as N_2O_3 is formed from NO_2 and NO at low temperatures, it decomposes again on warming into these components: $N_2O_3 \rightleftharpoons NO_2 + NO$. It is not ordinarily stable in the gaseous state, but appears only in the completely decomposed condition, as is obvious from the brown colour of the NO_2 present. In certain solvents, however, the compound is stable at somewhat higher temperatures, since the concentration at the normal pressure may then be higher than in the gaseous state. The molecular formula in glacial acetic acid corresponds approximately to N_2O_3. The existence of this substance in cold water may be recognised by the blue colour of the solution; *e.g.* if metallic silver is dissolved in cold nitric acid, the solution assumes a blue coloration similar to that of copper sulphate. The trioxide does not dissociate at room temperature in the gaseous state when perfectly dry.

Nitrogen dioxide combines not only with NO molecules, but also with molecules of the same kind. It polymerises to double molecules, $2NO_2 \rightleftharpoons N_2O_4$. Depolymerisation begins at the melting point of N_2O_4 (ca. $-12°$), and it is recognisable by the change in colour. The dimeric N_2O_4 is colourless, and the monomeric NO_2 deep brown; on heating, the gas becomes reddish brown, and at about $180°$ is almost black. The position of the equilibrium can be very accurately determined.[2] The decomposition at various temperatures is as follows:

Temp. . .	$26.7°$	$49.6°$	$70°$	$80.6°$	$111.3°$	$135.0°$
Per cent. NO_2 .	20.0	40.0	65.6	76.6	92.7	98.7

At higher temperatures it decomposes further into NO and O (*cf.* table,

[1] Briner, *J. Chim. Phys.*, 1913, 11, 597.
[2] L. and E. Natanson, *Wied. Ann.*, 1885, 24, 454.

p. 670). N_2O_4 preserves its bimolecular condition in glacial acetic acid solution.

At low temperatures N_2O_4 forms colourless crystals, which melt at $-11°$ to $-12°$; the yellow coloration then appears, and increases with rising temperature. The deep brown liquid, which contains considerable quantities of NO_2, boils at about $26°$. This boiling point remains constant, since the equilibrium between NO_2 and N_2O_4 is set up instantaneously.

Nitrogen trioxide forms a deep blue liquid, which boils at $3.5°$ with complete decomposition into NO and NO_2, and solidifies below $-100°$ to blue crystals. The melting-point data given in the literature on the subject are not in agreement, but it appears to melt between $-103°$ and $-112°$.

Nitric oxide is a difficult gas to condense. It also shows no tendency to polymerise. It boils at $-142.5°$ and solidifies at $-150°$ to a snowy mass. All three substances in the liquid condition are very bad conductors of electricity. They are not capable of dissolving salts, and NO itself only dissolves in liquids with difficulty. Water takes up one-twentieth, alcohol one-third of its volume of it. NO_2 is decomposed by water (*cf.* p. 674).

These compounds can enter complexes, but not so readily as ammonia or water (*cf.* p. 282 *et seq.*). The number of molecules which can form part of a complex is very limited (*cf.* p. 677).

The chemical properties of these oxides of nitrogen depend primarily on their reduction, secondly on their oxidation, and thirdly on their power to form addition products. Since N_2O_3 exists only at very low temperatures, it behaves otherwise like a mixture of NO and NO_2, so that it need not be specially discussed. The reduction of NO and NO_2 to N_2O or NH_3 has already been considered (pp. 609 and 666). It may be added that the reduction of NO_2 to ammonia takes place more easily than that of NO, mainly because the primary reduction to NO occurs easily with the liberation of energy, which is utilised in the further reduction. NO can be reduced to nitrogen by hydrogen (or ammonia), but only at higher temperatures, when explosion occurs, while NO_2 may be converted into ammonia by means of hydrogen at room temperature if contact materials (Pt, Ni, Co) are present. As can easily be understood, the oxidation by NO_2 is more energetic than that brought about by NO, although the latter is more strongly endothermic; thus NO_2, unlike NO, is able to oxidise carbon monoxide at the ordinary temperature. The decomposition of NO with the elimination of oxygen is subject to a retardation similar to that which occurs with N_2O, which it resembles in its gradual oxidising actions. The dissociation only proceeds to any extent after it has been induced by powerful local heating, but once started more heat is generated; moderate heating is insufficient. For this reason

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These compounds can enter complexes, but not so readily as ammonia or water (cf. p. 282 et seq.). The number of molecules which can form part of a complex is very limited (cf. p. 677).

The chemical properties of these oxides of nitrogen depend primarily on their reduction, secondly on their oxidation, and thirdly on their power to form addition products. Since N_2O_3 exists only at very low temperatures, it behaves otherwise like a mixture of NO and NO_2, so that it need not be specially discussed. The reduction of NO and NO_2 to N_2O or NH_3 has already been considered (pp. 609 and 666). It may be added that the reduction of NO_2 to ammonia takes place more easily than that of NO, mainly because the primary reduction to NO occurs easily with the liberation of energy, which is utilised in the further reduction. NO can be reduced to nitrogen by hydrogen (or ammonia), but only at higher temperatures, when explosion occurs, while NO_2 may be converted into ammonia by means of hydrogen at room temperature if contact materials (Pt, Ni, Co) are present. As can easily be understood, the oxidation by NO_2 is more energetic than that brought about by NO, although the latter is more strongly endothermic; thus NO_2, unlike NO, is able to oxidise carbon monoxide at the ordinary temperature. The decomposition of NO with the elimination of oxygen is subject to a retardation similar to that which occurs with N_2O, which it resembles in its gradual oxidising actions. The dissociation only proceeds to any extent after it has been induced by powerful local heating, but once started more heat is generated; moderate heating is insufficient. For this reason

burning sulphur and feebly burning phosphorus, the combustion temperatures of which are not very high, are extinguished in NO; but brightly burning phosphorus, glowing carbon or boron and strongly heated metals evolve sufficient heat to continue the decomposition, and then burn in NO as in free oxygen. NO_2, on the other hand, yields at least one oxygen atom at fairly low temperatures, and hence reacts under these conditions; the oxygen atom liberated reacts immediately, and the energy produced by its liberation serves to make the decomposition proceed more briskly. The effects of combustion in NO_2 are therefore exactly comparable to those in free oxygen, except that besides the oxides of metals some nitrite and nitrate are also formed.

Nitric oxide is very easily oxidised; it combines with free oxygen spontaneously and the colourless gas is converted into the brown NO_2. Other oxidising agents, such as hydrogen peroxide, permanganate, lead or manganese dioxides, nitric acid or hypochlorous acid, act similarly and oxidise it at once. In this way, in the presence of an adequate quantity of the oxidising agent, NO_2 is formed, or if water is present, HNO_3.

Nitrogen dioxide is converted into nitric acid by a mixture of water and air. In presence of water, it behaves as follows: $4NO_2 \longrightarrow N_2O_3 + N_2O_5$. The N_2O_5 formed is immediately converted into its hydrate, nitric acid, whilst N_2O_3 undergoes its characteristic decomposition into NO_2 and NO. Now, NO adds on oxygen with ease and can therefore be converted into NO_2, which again undergoes decomposition into N_2O_5 and N_2O_3, until finally it is all converted into nitric acid.

The conversion of oxides of nitrogen into nitric acid by the action of water and atmospheric air takes place best in alkaline solution. The gases produced by the arc process, in particular, which are rich in air, are therefore passed into a medium which is able to absorb the nitric acid immediately by neutralising it (lime). If NO_2 is passed into alkali without the presence of excess air, a mixture of nitrite and nitrate is formed, for the N_2O_3 develops its acid-anhydride property and is not decomposed into NO_2 and NO:

$$2NO_2 + H_2O \rightleftharpoons HNO_2 + HNO_3.$$

N_2O_4 naturally behaves in the same way as NO_2, but at a low temperature the decomposition of the N_2O_3 formed in this way may be avoided. If N_2O_4 is decomposed by a little water at $-20°$, two layers are formed: the upper one, pale green and consisting mainly of nitric acid which has dissolved some of the oxides of nitrogen, and the lower, deep green, consisting mainly of N_2O_3 containing some nitric acid. The same colorations are obtained with red, fuming nitric acid on continuously increasing the water content at about $0°$, even when no liquid N_2O_4 is present.

The mechanism of this process is best explained from a consideration of the equilibrium between the oxides of nitrogen, oxygen and water. After sufficiently long contact with excess air, nitrous fumes contain NO_2, or more strictly:

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3. $3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$, or simply decompose into the anhydride and water:

4. $2HNO_2 \rightleftharpoons N_2O_3 + H_2O$, when the anhydride then splits up further:

4a. $N_2O_3 \rightleftharpoons NO_2 + NO$. The last system then reverts to 1 if there is excess oxygen:

5. $2NO + O_2 \longrightarrow 2NO_2$. From the equilibria 1-3 the general equation,

6. $3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO$ can be constructed.

For 4, it is essential to know whether water is present in large or small quantities. If sufficient water is present (e.g. in 30-50 per cent. nitric acid) very little of the HNO_2 is dehydrated and the amount of N_2O_3 formed is not large, and thus in 4a not much NO_2 is produced; it is, however, formed according to 6, since NO is able to reduce the nitric acid to an increasing extent as the temperature rises. On the other hand, according to 6, the greater the partial pressure of the NO_2 becomes the stronger one expects the nitric acid to be.

If, on the contrary, small quantities of water are present, the formation of NO_2 according to 4 and 4a plays an important part, especially as the nitric acid combines with a portion of the water with the formation of a hydrate, thus further diminishing the quantity of water available:

7. $HNO_3 + 3H_2O \rightleftharpoons HNO_3, 3H_2O$;

8. $HNO_3, 3H_2O + 2HNO_3 \rightleftharpoons 3(HNO_3, H_2O)$.

For that reason 2 is also driven farther to the left to increase the formation of water, when N_2O_4 is also formed, resulting in red, fuming nitric acid. On the other hand, the quantity of N_2O_3 is diminished, and with it its decomposition and the formation of NO, and hence the production of nitric acid, which practically stops at about 78 per cent. HNO_3.

When there is not an adequate excess of oxygen, which produces NO_2 according to 5, and which drives 4a and therefore 4 to the left, the nitric acid obtained has a green to blue coloration, due to the N_2O_3 present. In this case air cannot be employed instead of oxygen, since owing to the presence of nitrogen it keeps the partial pressure of the NO_2 too low.

If liquid N_2O_4 is added to 8, two layers are formed, consisting of HNO_3 dissolved in N_2O_4, and the undissolved HNO_3 aq. in a diluted condition. The N_2O_4 taken up by the acid gives an equilibrium to the right-hand side of 2, and so finally 98-99 per cent. nitric acid is obtained.

Constitution.—The formulae of these oxides must be considered with reference to the number of valency electrons available for combination, e.g.:

N_2O,

$\overset{-}{N^4}\!\!\equiv\!\!\overset{++}{O}\!\!\equiv\!\!\overset{-}{N^4}$

$O^4\!\!\underset{\diagdown}{\overset{\diagup}{\Vert}}\!\!\overset{N^2}{\underset{N^2}{}}$

$\overset{-}{N^4}\!\!\equiv\!\!\overset{+}{N}\!\!\equiv\!\!\overset{-}{O^4}$

NO,

$\overset{-\frac{1}{2}}{N^8}\!\!\equiv\!\!\overset{+\frac{1}{2}}{O^3}$

N_2O_3,

$O^4\!\!\equiv\!\!N^2\!\!=\!\!O^4\!\!=\!\!N^2\!\!\equiv\!\!O^4$

N_2O_5,

$\overset{\overset{\overline{O}^6}{\diagdown}}{\underset{O^4\diagup}{}}N\!\!=\!\!O^4\!\!=\!\!\overset{+}{N}\overset{\overset{\overline{O}^6}{\diagup}}{\underset{\diagdown O^4}{}}$

burning sulphur and feebly burning phosphorus, the combustion temperatures of which are not very high, are extinguished in NO; but brightly burning phosphorus, glowing carbon or boron and strongly heated metals evolve sufficient heat to continue the decomposition, and then burn in NO as in free oxygen. NO_2, on the other hand, yields at least one oxygen atom at fairly low temperatures, and hence reacts under these conditions; the oxygen atom liberated reacts immediately, and the energy produced by its liberation serves to make the decomposition proceed more briskly. The effects of combustion in NO_2 are therefore exactly comparable to those in free oxygen, except that besides the oxides of metals some nitrite and nitrate are also formed.

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$\overset{-\frac{1}{2}}{N^3} \equiv \overset{+\frac{1}{2}}{O^3}$

N_2O_3,

$O^4 \equiv N^2 = O^4 - N^2 \equiv O^4$

N_2O_5,

$\overset{\overline{O}^6}{\underset{O^4}{}} N = O^4 = \overset{+}{N} \overset{\overline{O}^6}{\underset{O^4}{}}$

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Constitution.—The formulae of these oxides must be considered with reference to the number of valency electrons available for combination, *e.g.*:

There is particular difficulty in formulating the molecules NO, NO_2 and NO_3, which contain an odd number of electrons, but NO and NO_2 (monomeric) are paramagnetic, in agreement with the odd number of valency electrons present in the molecule. Electron diffraction measurements on the oxides do not yield conclusive results, for the scattering powers of oxygen and of nitrogen are approximately equal. It cannot be determined, therefore, if N_2O is NNO or NON, but Bailey and Cassie[1] consider that the molecule is best represented as $N \rightleftharpoons N = O$, i.e. $\bar{N}^4 \equiv \overset{+}{N} \equiv O^4$. Accepting this formula, results of electron diffraction indicate that N_2O might be considered as a resonance form of this and $N^2 \overset{+}{\equiv} N = \overset{-}{O}^6$, i.e. $N \equiv N \longrightarrow O$. Furthermore, the molecule has zero dipole moment, as for two linear structures. The physical properties of this gas and of carbon dioxide are very similar; both contain the same total number of valency electrons, and both are linear resonance structures (see p. 799).

The difficulties in interpreting the available data regarding NO and NO_2 largely disappear, however, if we accept the conception of the three-electron bond (see p. 359, structure of ClO_2). NO is then seen to be a resonance hybrid of $\cdot \ddot{N}$—$\ddot{O}$: and $^-: \ddot{N}$—$\ddot{O} \cdot^+$ which may be written :N⫴O:. Similarly NO_2 is written

$$N \begin{matrix} \diagup\!\!\diagup O \\ \diagdown\!\!\diagdown O \end{matrix}$$

, which repre-

sents resonance between two structures

$$N \begin{matrix} \diagup\!\!\diagup \ddot{O}: \\ \diagdown\!\!\diagdown \ddot{O}: \end{matrix} \quad , \quad N \begin{matrix} \diagdown\!\!\diagdown \ddot{O}: \\ \diagup\!\!\diagup \ddot{O}: \end{matrix}$$
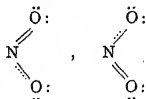
In both cases the resonance energy of the three-electron bond stabilises the molecule; for NO, this increased stability is sufficient to prevent polymerisation to N_2O_2, but NO_2, as is well known, readily polymerises to N_2O_4. The structure of the latter may be

$$^-:\ddot{O} \begin{matrix} \\ \diagdown \\ \diagup\!\!\diagup \end{matrix} \overset{+}{N}\!-\!\overset{+}{N} \begin{matrix} \diagup\!\!\diagup \ddot{O}:^- \\ \diagdown\!\!\diagdown \end{matrix} \quad \text{or} \quad ^-:\ddot{O} \begin{matrix} \\ \diagdown \\ \diagup\!\!\diagup \end{matrix} \overset{+}{N}\!-\!O \begin{matrix} \diagup \\ \diagdown \end{matrix} \ddot{N}\!=\!\ddot{O}:$$
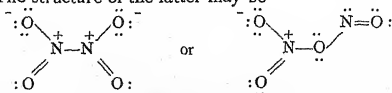
N_2O, however, is a resonance hybrid of

$$:\ddot{N}\!=\!\overset{+}{N}\!=\!\ddot{O}: \quad \text{and} \quad :N\!\cong\!\overset{+}{N}\!-\!\ddot{O}:^-,$$
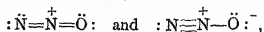
with small contributions by slightly less stable structures.

[1] *Physical Rev.*, 1932, ii., 39, 534.

The suggested structure of N_2O_3 is in agreement with its chemical behaviour, and the constitution can oscillate between

$$O = N\!-\!O\!-\!N = O \rightleftharpoons O\!-\!N\!\!\overset{\displaystyle O}{\diagup}\!\!\diagdown N\!-\!O \rightleftharpoons O = N\!-\!\overset{\displaystyle O}{\overset{\uparrow}{N}} = O,$$
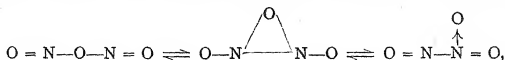
for the deep blue colour shows that loosely attached electrons are present, leading to tautomerism. The method of formation from $NO + NO_2$ is clear, as also its decomposition into these oxides.

Complex Compounds.—NO is more capable of addition reactions than NO_2. It is true that some addition compounds of NO_2 have been described, which are formed when the chlorides of iron, bismuth or antimony in the solid condition are acted upon by NO_2, and to which formulae like $FeCl_3, NO_2$ are given, but their existence is still questionable. The very interesting addition products (nitro-metals) which are formed by passing NO_2 over finely divided metals, have formulae, according to Sabatier and Senderens,[1] of the types $2Cu.NO_2$, $4Ni.NO_2$, $2Co.NO_2$. Park and Partington have shown [2] that the first action of NO_2 on copper gives cuprous oxide, $2Cu + NO_2 \longrightarrow Cu_2O + NO$, the cuprous oxide subsequently absorbing up to 33 per cent. of its weight of NO_2. The nitrogen dioxide can be removed by heating or by carbon tetrachloride at $65°$-$70°$. Hence it is probable that all these bodies are adsorption products, though the extent of the adsorption is remarkable. NO_2 does not combine directly with halogens (*cf.* p. 702), while NO, in the same way that it combines rapidly with O_2 or NO_2, also unites, though less readily, with Cl_2, still less so with Br_2, with the formation of gaseous nitrosyl halides (*cf.* p. 682). NO and NO_2 also form a compound of the formula $N_2O_3, 2SO_3$, but this is probably not a mere addition compound, but may be considered as $NO.O.SO_2.O.SO_2.O.NO$ or $(NO)_2(S_2O_7)$ (see p. 683). It forms white crystals which are decomposed by water.

Nitric oxide, on the other hand, occurs as a neutral group in salts, and combines with those of metals of the iron group, giving a series of compounds distinguished by their vivid colours. These compounds differ from the ammines and hydrates in that not more than one NO residue usually exists in the complex. The presence of other neutral groups besides the NO is not precluded, but is even of assistance in the formation of the complex.

The salt-like "*nitroso-compounds*" may be divided into two groups : those which decompose easily into their components by a reversible reaction, and those which are distinguished by their great stability. The former class of compounds has been especially studied by Manchot [3] and by Kohlschütter.[4] The best known compounds of this class, those

[1] *Ann. Chim. Phys.*, 1896 (7), 7, 348. [2] *J. Chem. Soc.*, 1924, 125, 72.
[3] *e.g. Ber.*, 1914, 47, 1601. [4] *e.g. Ber.*, 1911, 44, 1423.

with iron salts, are the basis of the usual method of detection of nitric acid with ferrous sulphate (brown ring test).

The addition of the NO takes place when the gas is passed into solutions of ferrous and cupric salts. The compound is decomposed on warming and the NO may be driven off without any change in the metallic salt (though $Cr^{..}$ salts combined with NO are converted to $Cr^{...}$ compounds). The amount of NO absorbed never exceeds 1 mol. per atom of metal, and is usually less; it falls with the pressure and temperature, and increases up to a certain limit with the salt concentration. It is also increased in the presence of solvent media which diminish dissociation (alcohol, conc. acids).

Three types of compounds with ferrous salts are known—brown, red and green. Their nature is elucidated to some extent by the motion of the coloured portion on electrolysis, when the brown colour goes to the cathode, the green to the anode, and the red apparently does not wander at all. These facts are explained by considering that the salts of this metal, especially the halogen salts, are able to occur in the bimolecular form $(FeCl_2)_2$, e.g. as the ferrous salt of a ferrochloro-acid $[FeCl_4]H_2$, viz. $[FeCl_4]Fe$. Here the $[Fe(Cl_4)]$ ions combine with the NO with formation of a green compound; the $Fe^{..}$ ions give a brown coloration, and the red compounds which are not mobile and which are formed in the presence of concentrated sulphuric acid, have a constitution which has not yet been explained. These red salts (like the deep blue cupric compounds) are very similar to those of nitrosisulphonic acid (cf. p. 638), which are prepared in a somewhat similar way, but they can be distinguished from one another by their spectra. The brown and red salts may be isolated in the solid condition, but the crystals are very unstable, the most stable being the phosphate[1] $FeHPO_4$, NO and the selenate[2] $FeSeO_4$, NO, $4H_2O$. In the cupric compounds only one type appears to exist, corresponding to the green ferrous salt. The solution is deep blue to violet. Ordinary blue cupric salt solutions do not absorb NO; only the green or brown concentrated solutions of copper bromide or chloride, or dilute solutions which have assumed these colours on the addition of acids, have this property. These copper solutions contain the complex anion $[Cu(Cl_4)]''$, so that only this ion and not the cupric ion $Cu^{..}$ can combine with NO. Ferric salts also give deep red addition compounds in sulphuric acid solution, to which the formula $Fe(SO_4)_3.4NO$ is given. In the solid condition, neither cupric nor ferrous compounds combine with nitric oxide, with the exception of ferrous phosphate; but $MnCl_3$. NO and $CuCl_2$. NO can be made by the action of NOCl on $MnCl_2$ and $CuCl$ respectively[3]; the nitrosyl compounds are therefore of the cupric type (see p. 681), whereas the carbonyl compounds, which are analogous in many ways, are formed from univalent copper compounds, e.g. $Cu(CO)Br$. The solid chlorides of tervalent metals such as aluminium, iron and bismuth, on the other hand, take up gaseous NO, to give coloured powders ($FeCl_3$. NO red, $BiCl_3$. NO yellow), but the NO is easily given up again (Thomas). Manchot has also prepared palladous compounds of the formula PdX_2. $2NO$. The dark red addition product of nitric oxide and hydrogen chloride, which is formed at the temperature of liquid air, belongs to the same class of compounds.

Those compounds in which the NO is linked with other neutral groups, such as NH_3 or CN, to a metal atom are considerably more

    [1] Thomas, *Compt. rend.*, 1895, **120**, 447; **121**, 128, 204; cf. Manchot, *loc. cit.*
    [2] Manchot and Linckh, *Z. anorg. Chem.*, 1924, **140**, 37.
    [3] H. Gall and H. Mengdehl, *Ber.*, 1927, **60**, 86.

stable. Here, besides the very stable compounds of iron, those of cobalt are known, and may be considered as cobaltammines, in which an ammonia molecule is replaced by NO. They are formed when NO is passed into ammoniacal solutions of cobaltous salts, and have the formula:

$$\left[Co\begin{array}{c} NO \\ (NH_3)_5 \end{array} \right] X_2.$$
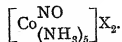
They appear in two different modifications, a black and a red, the red form being possibly dimeric and the black monomeric.[1] If the halogen salts are employed, the black series is mostly produced, while if the sulphates or nitrates are used, the red series appears; the black series is spontaneously converted into the red, but not the red into the black. The method of linking of the NO group recalls that of oxygen in the oxy-cobaltammines (cf. p. 321); the compounds can easily be changed back again into cobaltous salts, and, on the other hand, they show their relation to the cobaltic salts on treatment with acid, since with hydrochloric acid they form the purpureo-compound $[Co^{III}(NH_3)_5Cl]Cl_2$, nitric oxide being given off. It may be supposed that there is a continual change from bi- to tervalent cobalt in the compound, and it is possibly this which causes the black colour of the class. Compounds of variable valency are often deeply coloured (cf. p. 757). Sidgwick and Bailey[2] (see also p. 681) consider that these compounds are not of the true nitrosyl type, in which NO contributes three electrons to the valency shell of the metal, but are nitroso-salts containing the bonds $M\text{---}N=O$, in which Co is tervalent and covalently linked to nitrogen just as it is covalently linked to Cl in $[CoCl(NH_3)_5]Cl_2$.

The complex iron compounds containing NO groups are mainly sulphides or thiosulphates, and are distinguished by their deep black or reddish brown coloration. The compounds which are called Roussin's salts, after their discoverer,[3] have a very complicated structure. The potassium salts are of the types:

I. $K_2[Fe_2S_2(NO)_4]$ II. $K[Fe_4S_3(NO)_7]$

III. $K[Fe(S_2O_3)(NO)_2]$ IV. $K_3[Fe(S_2O_3)_2(NO)_2].$
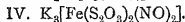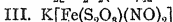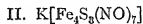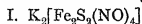
I. probably contains 2 sulphur bridges uniting the 2 Fe atoms, the 4 NO groups being directly linked to Fe. III. is possibly dimeric, the iron atoms being bridged through S of the thiosulphate group; II. appears to be tetrahedral and related in type to $Co_4(CO)_{12}$ (see p. 794). IV. may be monomeric with each of the 4 groups within the complex directly linked to Fe.

Of these compounds, III. is formed by passing NO into a solution of ferrous sulphate containing thiosulphate. Compound I. is formed by treating II. with

[1] Werner and Karrer, *Helv. Chim. Acta*, 1918, **1**, 54; Milward, Wardlaw and Way, *J. Chem. Soc.*, 1938, 233.

[2] *Proc. Roy. Soc.*, 1934, [A] **144**, 531.

[3] *Cf.* Hofmann and Wiede, *Z. anorg. Chem.*, 1895-96, 8-11.

alkali; and II. may be formed in numerous ways, *e.g.* by passing NO into a suspension of FeS in an alkali sulphide, followed by treatment with dilute acid, or by dropping ferrous sulphate into a solution of nitrite and sulphide mixed; from a suspension of ferrous hydroxide by the action of NO and CS_2, etc. The mechanism of their formation has not yet been explained. The alkali salts are not very soluble, and the salts of the heavy metals are not known, though some esters have been prepared, *e.g.* $(C_2H_5)_2Fe_2S_2(NO)_4$ and $(C_2H_5)_2Fe_2S_2(NO)_4$ from ferrous mercaptide and nitric oxide.[1] Molecular weight determinations of these agree with the double formula and from measurement of magnetic susceptibility of I., which Cambi and Szegö[2] have undertaken, it is considered that the bimolecular form is correct, one iron atom being bivalent and the other tervalent, and that three −NO groups are in the complex as univalent radicals and a fourth as a molecule.

Manchot[3] also obtained, with nickel and cobalt, complex salts of the general formula $K_2[M(S_2O_3)_2(NO)_2]$. These compounds are formed when the metal salts are kept in an atmosphere of NO in the presence of alkali thiosulphates. The cobalt compound is brassy in appearance, the nickel compound blue; both can be dissolved in water and recovered from the solution and are generally quite stable. The mode of formation is probably analogous to the following reaction of the metallic mercaptides :

$$Ni(SC_2H_5)_2 + 2NO \longrightarrow Ni(SC_2H_5)_2 . 2NO \longrightarrow NiSC_2H_5 . NO + NO . SC_2H_5.$$
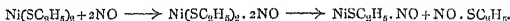
An unstable intermediate compound is formed, which then loses nitrosyl mercaptide; the last breaks down to 2NO and $C_2H_5S . SC_2H_5$. Ferrous and cobaltous mercaptides react similarly to form $Fe(Co)SC_2H_5 . 2NO$ and these highly coloured products are non-polar, for they are soluble in organic solvents and have low melting points.

The thiosulphate reacts as follows :

$$Ni(S . SO_3K)_2 + 2NO \longrightarrow Ni(NO)S . SO_3K + NO . S . SO_3K$$
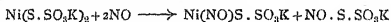
the latter compound breaking down to tetrathionate, which is obtained in good yield :

$$2NO . S . SO_3K \longrightarrow 2NO + K_2S_4O_6.$$

Sodium nitroprusside belongs to this class of iron nitroso-compounds. This cyano-compound $\left[Fe \begin{array}{c} (CN)_5 \\ NO \end{array} \right] Na_2$ is formed when potassium ferrocyanide $K_4Fe(CN)_6$ is warmed with dilute nitric acid, and afterwards neutralised with soda. It crystallises in somewhat brownish red crystals, and has been described on p. 309. Manchot and Schmid[4] have prepared the manganese analogue of nitroprusside, $[Mn(CN)_5NO]Na_2$, by the action of NO on a solution of the double manganese cyanide. It forms blue-violet crystals which give a purple solution in water. It would appear that the same group of metals which form addition compounds with CO can also do so with NO.

$K_2[Ru(NO)Cl_5]$, which is obtained by the action of nitric acid on $K_2[RuCl_5 . H_2O]$ (see p. 304) or from $[RuCl_3 . NO]$ and 2KCl, is very stable, but is decomposed by aqueous ammonia forming $[Ru(NO)(OH)(NH_3)_4]Cl_2$. This gives $[Ru(NO)Cl(NH_3)_4]Cl_2$ and

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[1] See Hofmann and Wiede, *loc. cit.*
[2] *Atti. R. Accad. Lincei*, 1931 [vi], **13**, 168.
[3] *Ber*, 1926, **59**, 2445.   [4] *Loc. cit.*, 2360.

$[Ru(NO)H_2O(NH_3)_4]Cl_3$ with hydrochloric acid. $K_2[Os(NO)Cl_5]$ is formed by a different series of reactions; potassium osmichloride, $K_2[OsCl_6]$, formed by heating osmium and potassium chloride in a stream of chlorine, reacts with potassium nitrite to give $K_2[Os(NO_2)_6]$, which on decomposition with hydrochloric acid yields $K_2[Os(NO)Cl_5]$.

Sidgwick and Bailey[1] have considered the formulation of these nitrosyl compounds. They point out their similarity with the carbonyls (see p. 793), and consider in each case that there is a triple bond uniting the carbon or nitrogen and oxygen:

$$-C\equiv O \qquad \text{and} \qquad -N\equiv O.$$
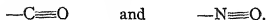
The 5-electron linkage in free NO becomes therefore a 6-electron bond in the nitrosyls. Combination is postulated as follows:

$$\dot{M} : N \overset{\cdot\cdot x}{\underset{xxx}{}} O \overset{x}{\underset{x}{}}$$
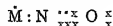
2 electrons obtained from N being shared with the metal M to form a co-ordinate link, and a further electron being transferred from N to M; summation of charges (p. 51) then gives $\overset{=}{M}-\overset{+}{N}\equiv\overset{+}{O}$ or $M \leftarrow N \rightleftharpoons O$; $NiSC_2H_5 . NO$ is accordingly

$$C_2H_5S-\overset{=}{Ni}-\overset{+}{N}\equiv\overset{+}{O}.$$
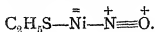
The NO group therefore contributes 3 valency electrons to the metal shell. Electron transference can also take place in certain cases to form polar compounds, such as $(NO)^+(ClO_4)^-$ (see p. 683).

Iron is bivalent, on these views, in the nitroprussides, for the valency shell of iron of 12 electrons is made up of 1 electron contributed by each of the 5 CN groups, 3 by NO, 2 by Fe and 2 transferred from the cation—or viewed in Main Smith's notation, the group is

$$(N^?\equiv C=)_{\overline{5}}^{----}Fe=\overset{+}{N}\equiv\overset{+}{O^2},$$
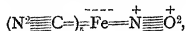
the resultant charge being -2, if iron is assumed to be bivalent.

The action of alkali or alkali sulphide, i.e. of OH' or SH' ions on nitroprussides to form $M_4[Fe(CN)_5NO_2]$ or $M_4[Fe(CN)_5NOS]$ is accounted for by the conversion of the $\overset{=}{Fe}-\overset{+}{N}\equiv\overset{+}{O}$ group, possibly by addition of the anions, via

$$\overset{==}{Fe}-\overset{OH\ OH}{N}\equiv O \qquad \text{and} \qquad \overset{==}{Fe}-\overset{SH\ SH}{N}\equiv O \qquad \text{to}$$

$$Fe-N\overset{\nearrow O}{\underset{\searrow O}{}} \qquad \text{and} \qquad Fe-N\overset{\nearrow O}{\underset{\searrow S}{}}$$
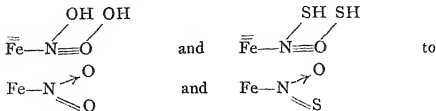
This involves the withdrawal of two electrons from the central atom, and consequently an increase in the electrovalency of the complex by 2; the iron throughout, however, remains bivalent.

[1] Proc. Roy. Soc., 1934, [A], 144, 521.

By the action of NO on metal carbonyls metallic nitrosyl-compounds which are not salts are formed.[1] Thus $Ni(CO)_4$ with NO gas forms a blue powder of $Ni(NO)_2$, which has an odour of almonds, is insoluble in water, but is soluble in chloroform, and decomposed by acids with evolution of oxides of nitrogen. It is stable at moderate temperatures but decomposes at 90° with a vivid emission of light. In iron and cobalt carbonyls only a portion of the CO is replaced by NO; they form red liquids, e.g. $Co(CO)_3NO$, m.pt. $-1°$, b.pt. 79° and $Fe(CO)_2(NO)_2$, m.pt. 18°, b.pt. 110°, which are stable to water and may be distilled at a moderate temperature with slight decomposition. In each of these compounds, assuming each molecule of CO to contribute 2 electrons and each NO to contribute 3 electrons, Fe and CO have each shells of 36 electrons, i.e. the Kr type.

$Fe(CO)_5$ heated with NO under pressure gives black crystals[2] of $Fe(NO)_4$. The relation $G - \dfrac{xm + 2y + 3z}{x} = x - 1$, which is similar to that which applies to the carbonyls (see p. 793), holds for all nitrosyls $M_x(CO)_y(NO)_z$.

The so-called *nitrosyl halides*, NOF, NOCl, NOBr, are probably not to be regarded as complex compounds. Of these, the chloride and bromide are formed by the addition of the halogens to NO : $2NO + Cl_2 \longrightarrow 2NOCl$; the fluoride can only be obtained by decomposing the chloride with AgF. The reaction between NO and F_2 gives no NOF, but takes place with the formation of nitryl fluoride, NO_2F (p. 702), and free nitrogen: $4NO + F_2 \longrightarrow 2NO_2F + N_2$ (nitryl bromide does not exist). NOBr undergoes decomposition even at the ordinary temperature; NOCl, on the other hand, is very stable to heat, but shows an abnormal density above 700°. It may be looked upon as the chloride of nitrous acid, NO . OH, and is the chief active constituent of *aqua regia*: $HNO_3 + 3HCl \rightleftharpoons NOCl + Cl_2 + 2H_2O$. In open vessels reaction is complete in the direction of the upper arrow, owing to the escape of the chlorine formed. If this is prevented by working in sealed tubes[3] a red liquid phase consisting of NOCl and liquid chlorine is formed, which with the aqueous acids gives a "stabilised" *aqua regia*. All three nitrosyl halides have a powerful halogenating action; their odour is also similar to that of the halogens. Nitrosyl chloride combines with $ZnCl_2$, $AlCl_3$, $FeCl_3$, $BiCl_3$, $AuCl_3$, $PtCl_4$, $SbCl_5$, etc., to give yellow double compounds each of which contains 1 mol. of NOCl, while the compounds with $SnCl_4$, $TiCl_4$, and $PbCl_4$ contain 2 mols. of NOCl.[4] These are possibly nitrosyl salts (see next section), e.g.

$$(NO)[AlCl_4] , (NO)[AuCl_4] , (NO)_2[SnCl_6] \text{ etc.}$$
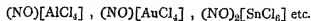
All the nitrosyl halides are gaseous at ordinary temperatures; their special properties are as follows:

NOF	.	B.pt. $-56°$	M.pt. $-134°$		Colourless.
NOCl	.	,, $-5\cdot8°$	,, $-61\cdot5°$		Yellow; liquid, yellowish red; solid, blood red.
NOBr	.	,, $-2°$	,, ?		Blackish brown.

[1] Mond and Wallis, *J. Chem. Soc.*, 1922, **121**, 32.

[2] Manchot and Enk, *Ann.*, 1929, **470**, 275 ; Hieber and Anderson, *Z. anorg. Chem.*, 1933, **211**, 132.

[3] Briner, *Bull. Soc. Chim. Belg.*, 1927, **36**, 79.

[4] H. Rheinbold and R. Wasserfuhr, *Ber.*, 1927, **60**, 732.

Nitrosyl Salts, Nitrosacidium Salts.—A most interesting class of compounds was described by Hantzsch and Berger[1] in which the NO group of nitrous acid forms a positive ion. These compounds are formed when nitric oxide is passed into concentrated strong acids or caused to combine with their anhydrides. The most important members of this class are:

$ClO_4 . NO$	$BF_4 . NO$	$O(SO_3)_2 . (NO)_2$
Nitrosyl perchlorate	fluoroborate	pyrosulphate
$HSO_4 . NO$	$HSeO_4 . NO$	$SO_3F . NO$
Nitrosyl sulphate (chamber crystals)	selenate	fluorosulphonate

Nitrosyl chloride is probably not to be classed among these substances. Nitroxyl perchlorate, $NClO_6$, has also been prepared.

These compounds are not non-polar as has been previously assumed, nor are they analogous to the acid anhydrides, but must be described by polar formulae of the type $NO\dot{}(ClO_4)\prime$, which, for instance, is found to be a binary electrolyte in nitromethane solution, and the corresponding sulphate is completely dissociated in sulphuric acid solution. The positive ion is $NO\dot{}$, combined with the negative ions $ClO_4\prime$ and $HSO_4\prime$. All these salts are decomposed by water, though when dry they are stable at moderate temperatures. The perchlorate, stable by itself, frequently oxidises organic compounds with explosion.[2] The pyrosulphate (see p. 677) forms white crystals melting at 217°. The selenate, made from SeO_3 and N_2O_3, is a white snowy mass. The most important compound of this type is the sulphate, the well-known chamber crystals (see p. 646). It is at once hydrolysed by water:

$$HO . SO_2 . \overbrace{ONO + H}^{} OH \longrightarrow HO . SO_2 . OH + HONO.$$

For many years this compound was supposed to have the formula of nitrosulphonic acid, $O_2N . SO_3H$, in which the nitrogen is directly joined to the sulphur atom, or at least that an equilibrium between the two forms existed. Hantzsch and Berger, however, have shown that it is exclusively the nitrosacidium salt $NO\dot{}(SO_4H)\prime$ and that even the assumption of a mixed anhydride formula like $HO . SO_2 . O . NO$ is untenable, as this would be a non-polar compound. In solutions which have not decomposed it has no nitrating action but gives nitroso-compounds. The NO form is suggested by its lack of colour, and its ionisation in sulphuric acid points to its saline nature. The formation of nitrosyl chloride from HCl and chamber crystals cannot be reconciled with the NO_2 formula:

$$SO_4H . \overbrace{NO + Cl}^{} H \longrightarrow NOCl + SO_4H_2.$$
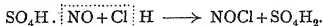
Nitrogen Pentoxide, N_2O_5.—Nitrogen pentoxide, the anhydride of nitric acid, cannot be obtained synthetically from the lower oxides

[1] *Z. anorg. Chem.*, 1930, **190**, 321.
[2] Hofmann and v. Zedtwitz, *Ber.*, 1909, **42**, 2021.

of nitrogen, since it is too easily decomposed. It can, however, be obtained if chlorine is passed over solid silver nitrate, when NO_2Cl is formed, which then gives nitrogen pentoxide with the excess nitrate:

$$NO_2 \underset{}{\overline{Cl+Ag}} NO_3 \xrightarrow{-AgCl} N_2O_5.$$
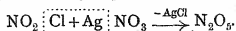
N_2O_5 may also be obtained by dehydrating nitric acid: $2HNO_3 \longrightarrow N_2O_5 + H_2O$. This dehydration must be carried out by the introduction of phosphorus pentoxide at the lowest possible temperature, on account of the ease with which N_2O_5 is decomposed. The N_2O_5 formed is then distilled off by gentle heat.

N_2O_5 forms colourless, transparent hygroscopic crystals, which may be kept for a long time at a low temperature, but which gradually decompose irreversibly at room temperature, thus: $N_2O_5 \longrightarrow 2NO_2 + O$. It has a vapour pressure of one atmosphere at $32 \cdot 5°$ and sublimes without much decomposition; it sometimes decomposes spontaneously with explosion. The gradual but complete decomposition of concentrated nitric acid is due to the presence of small quantities of free N_2O_5.

For nitrogen trioxide, NO_3, cf. p. 703.

Nitric Acid, HNO_3, and Nitrous Acid, HNO_2

These acids or their salts may be produced wherever nitric oxide is formed, provided oxygen and water are also present. All the synthetic methods of preparation of NO, N_2O_3 and NO_2 may therefore be used to obtain nitric and nitrous acids; the manner in which these acids are formed from the oxides of nitrogen has already been discussed (p. 674). The oxides formed by the union of nitrogen and oxygen or by the combustion of ammonia are passed into water with excess air, or better, absorbed by bases. The presence of nitrates and nitrites in rain water is due to the NO which is formed under the influence of electric discharge (lightning) in the atmosphere.

Further, certain kinds of bacteria synthesise nitrites and nitrates from the constituents of the atmosphere; others form ammonia from atmospheric nitrogen. A limited amount of this synthesis is carried out by the *Azotobacter* and *Clostridien* groups of bacteria, but from the point of view of agriculture the more important work is done by the nodule bacteria which inhabit the roots of the *Leguminosae*. Hence the planting of leguminous plants is equivalent to nitrogenous manuring of the fields. The mechanism of this fixation is probably as follows: The nitrogen in the living part of these bacteria is converted into ammonia by a putrefactive process; the ammonia is then oxidised by other bacteria into nitrous acid, which is immediately transformed into nitric acid by nitrate-forming bacteria. The nitrate thus formed acts as a plant food. The formation of the natural saltpetre deposits is probably largely due to the putrefaction of large masses of small

organisms in limbs of the sea which were shallow and rich in food materials, so that, with the action of suitable climatic conditions, ammonia and hence nitrites and finally nitrates were formed. Further, other bacteria can break down saltpetre into nitrites and ammonia (denitrifying bacteria), thus causing a loss in the nitrate content of the soil; but this loss is probably not great, as the nitrogen is utilised in the building-up of the living substance of the bacteria.

The oxidation of compounds of tervalent nitrogen such as ammonia, nitrides or cyanides to nitrates or nitrites can take place at temperatures well below a red heat with the aid of the oxygen of the air or of oxidising agents such as chlorate or sodium peroxide, provided water is excluded. A catalyst such as metallic silver or gold, or copper oxide, or particularly nickel oxide, facilitates the reaction.[1] For instance, the reaction

$$3KClO_3 + 2NH_3 \longrightarrow 2KNO_3 + KCl + Cl_2 + 3H_2O$$
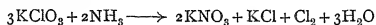
takes place below 200°, and urea, magnesium nitride or calcium cyanamide can be "nitrified" with sodium peroxide. If a stream of air containing 3 to 4 per cent. of ammonia is passed over a basic contact mass, oxidation takes place with considerable speed. NO and NO_2 are the sole products. Hence the reaction cannot be regarded as a mere removal of hydrogen from the nitrogen compound, as only traces of nitrogen and nitrous oxide are formed; it is rather to be regarded as an addition of oxygen in the first place, with subsequent elimination of hydrogen, so that the nitrogen is never actually free, thus:

$$NR_3 \longrightarrow (O_2)NR_3 \longrightarrow O_2NR + R_2 \longrightarrow RNO_2 \longrightarrow RNO_3.$$
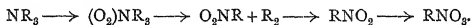
In the oxidation of sodamide in the air there is formed a peroxide, $O_2 . NaNH_2$, which in damp air gives sodium peroxide but in dry oxygen gives sodium nitrite. It is therefore probable that the technical oxidation of ammonia follows a similar sequence of reactions, as no nitrogen is liberated when the process is worked below 600°.

Since the nitrates may be more easily isolated by crystallisation than the nitrites, the latter are usually prepared subsequently from the nitrates. The oxygen may be removed, either by heat alone or by adding reducing agents such as carbon, metals, sulphides, etc., which are then converted into the oxides:

$$2KNO_3 + C \longrightarrow 2KNO_2 + CO_2, \qquad NaNO_3 + Pb \longrightarrow PbO + NaNO_2,$$
$$15KNO_3 + 2FeS_2 \longrightarrow 15KNO_2 + Fe_2O_3 + 4SO_3.$$
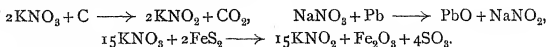
Nitric acid is stable, but nitrous acid rapidly undergoes decomposition into its anhydride and water; the anhydride splits up into NO_2 and NO, as described on p. 674, and the NO then escapes from

[1] Hofmann, Ber., 1926, 59, 204.

the solution. When dilute nitrite solutions are acidified the gases are not immediately evolved; on the addition of porous materials such as sand, pumice, etc., they are liberated, just as carbon dioxide which has been dissolved in water for a considerable time may likewise be removed by addition of substances which have a large surface. It may perhaps be assumed that the N_2O_3 remaining in supersaturated solutions hinders the complete decomposition of the HNO_2 into N_2O_3 and H_2O according to the law of mass action. The dilute aqueous solution of HNO_2 is only slightly yellow; it thus contains only a little free NO_2 and correspondingly little NO.

In order to obtain free nitric acid its salts are heated with a less volatile acid, usually with sulphuric acid; the reaction is completed to the stage

$$NaNO_3 + H_2SO_4 \longrightarrow HNO_3 + NaHSO_4.$$
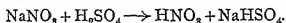
On heating the bisulphate obtained with more nitrate, further double decomposition occurs, but this does not proceed according to the equation: $NaNO_3 + NaHSO_4 \longrightarrow HNO_3 + Na_2SO_4$, since the necessary temperature lies so high that the nitric acid undergoes considerable decomposition (cf. pp. 669-70). Thus, methods which diminish the temperature of the distillation process diminish the quantity of NO_2 in the nitric acid produced. Hence sodium nitrate and not potassium nitrate is used, since the former decomposes at a lower temperature; the distillation may also be carried out in vacuo[1] when the distillation temperature is appreciably lower. It is not easy to obtain nitric acid altogether free from NO_2; but as this gas is so very volatile it is sufficient to blow a current of air through the solution in order to remove it.

The nitric acid obtained in this way is already fairly free from water and contains approximately 99 per cent. HNO_3. It cannot be altogether freed from water by this method, on account of the decomposition which it always undergoes into anhydride and water. However, the small water content is sufficient to repress this decomposition to a large extent owing to the effect of mass action, so that it goes no further. If the decomposition of the N_2O_5 present is prevented by keeping the acid in the dark, the concentration remains unchanged; if the acid is allowed to become brown by the decomposition of N_2O_5 the quantity of HNO_3 becomes increasingly less. A 60 per cent. acid (sp. gr. 1·4) undergoes decomposition very slowly.

It is possible, however, to obtain, at least temporarily, anhydrous 100 per cent. nitric acid as a colourless, transparent liquid, either by introducing the calculated quantity of solid N_2O_5 into the dilute acid or by freezing the latter.[2] It is not stable, for the reasons outlined

[1] Valentiner, Ber., 1892, 25, 878.
[2] Küster and Münch, Z. anorg. Chem., 1905, 43, 350.

above. It is not possible to obtain a very concentrated acid from a dilute one by distillation, as a constant boiling mixture is obtained as with hydrochloric acid (cf. p. 223). The curves of the elevation of the boiling point of water by nitric acid and that of nitric acid by water meet at about 121° under atmospheric pressure. The mixture which distils over then contains 68·0 per cent. acid, whilst under 1220 mm. pressure a 68·6 per cent. acid distils. The anhydrous acid begins to boil at 86° (at 35° under 20 mm.), but the boiling point then begins to rise owing to decomposition.

The acid of constant boiling point corresponds approximately to the formula $HNO_3, 2H_2O$, but it does not represent an individual dihydrate.

Mixtures with a varying water and nitric acid content show characteristic solidifying temperatures according to the accompanying curves.[1]

There are two maxima with a nitric acid content of 25 and 50 mols. per cent., which correspond to the formulae $HNO_3, 3H_2O$ and HNO_3, H_2O. The curve ends on one side at the freezing point of water, 0°, and on the other side at that

FIG. 58.—Freezing point curve of nitric acid.

of pure nitric acid −41·3°, and shows besides three eutectics as minima. The hydrates thus identified are also reflected, a little less sharply, in the conductivity of nitric acid at various dilutions, in the variations in the expansion of such acids on heating, and in many other physical properties, but not in the viscosity.

The viscosity certainly shows a maximum at one concentration, which corresponds to the nitric acid of constant boiling point and the apparent dihydrate ; but owing to the dissociation which takes place simultaneously, the composition of the solution does not correspond to this hydrate. The viscosity (η) at 15°, referred to water at 0° as unity, is as follows :

Mol. per cent. HNO_3 .	98·5	82	70	65	50	30	10
η	0·55	1·04	1·28	1·30	1·14	0·82	0·67

The great affinity of the pure acid for water is also obvious from the development of heat when the liquids are mixed and from the way in which it fumes strongly in damp air. As with hydrochloric acid, this phenomenon is explained by the volatile acid raising the boiling point of the water vapour previously present in the atmosphere, so that it is no longer able to remain in the gaseous

[1] Küster and Kremann, Z. anorg. Chem., 1905, 41, 1.

condition; in addition to this, there is the effect of the chemical union with the water.

There is very little basis for accepting the formulae of orthonitric acids for the hydrates, e.g. H_3NO_4, instead of the formula for HNO_3, H_2O, though salts of this acid and also of orthonitrous acid, H_3NO_3, can be prepared.[1]

The pure concentrated acid has a specific gravity of 1·52-1·54. This is lowered by the addition of water as follows:

Per cent. HNO_3 .	.	90	80	70	60	50	40	30	20
d_{15} .	. . .	1·495	1·460	1·444	1·393	1·334	1·267	1·200	1·132

Constitution.—Nitrous and nitric acids each behave according to two different formulae. This can be recognised qualitatively from the variety of their reactions under different conditions; e.g. solutions of the neutral salts have almost no oxidising action, while the free acids can display great oxidising power. The reasons for this have been made clear by spectroscopic investigations. The alkali salts and esters of nitric acid show quite different absorption spectra in the ultra-violet, and must therefore be differently constituted. The concentrated acid shows a spectrum which is identical with that of the esters, while that of the dilute acid is the same as that of the alkali salts. Acids of medium concentration give both spectra together. Now the salts certainly dissociate in solution and the esters are undissociated, but the mere process of dissociation into ions of a similar structure, according to Hantzsch, causes no change in the spectrum; a formula must therefore be assumed for the salts (and for dilute nitric acid) which permits of dissociation (I.), and for the esters and the concentrated acid a formula which excludes dissociation (II.):

$$\text{I.} \quad \left[N(O_3) \right] H. \qquad \text{II.} \quad \left[N\frac{(O)_2}{OH} \right].$$
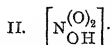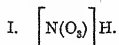
Both forms are present together in nitric acid of medium concentration. Nitric acid is thus a true acid in dilute solution, and a neutral complex when concentrated. In the former the hydrogen atom stands in the same relation to all or at least to two of the oxygen atoms; in the second it is more closely attached to one oxygen atom.[2] The vapour of the acid gives the same spectrum as the liquid concentrated acid, showing that the dissociating form is not present.

Hantzsch[3] has modified and extended this conception. Free nitric acid does not exist as HNO_3, but only as the hydroxonium compound $NO_3 \cdot OH_2$. This is present in aqueous solution, while in non-dissociating solvents the pseudo-form only is found. The act of dissociation is dependent on the association of a solvent molecule

[1] Zintl and Morawertz, *Z. anorg. Chem.* 1938, 236-237, 372.
[2] Schäfer, *Z. anorg. Chem.*, 1919, 97, 285 ; 98, 70.
[3] Hantzsch, *Ber.*, 1925, 58, 941 ; 1928, 61, 1328.

with the H˙ ion; indeed the dissociated form is really a salt in which water is attached to the H˙ ion in the same way that NH_3 is utilised in the formation of the ammonium salts. A third conception is necessary in order to describe completely the behaviour of this acid. In moderately dilute solutions nitronium nitrate, $[H_2NO_3]˙\ NO_3′$ is present, and in this dimeric form of nitric acid one of the NO_3 groups is present in a complex cation. Hantzsch was able to show that such a complex does actually move towards the cathode on electrolysis. This happens in the compounds formed with the stronger perchloric acid in which the nitric acid has a basic function:

$$HClO_4 + HNO_3 \longrightarrow [H_2O_3N]ClO_4$$
$$2\,HClO_4 + HNO_3 \longrightarrow [H_3O_3N](ClO_4)_2$$
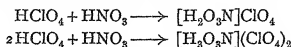
These solid products can be isolated by the interaction of anhydrous nitric and perchloric acids. A similar salt formation takes place when SO_3 acts on concentrated nitric acid when nitronium bisulphate, $[H_3O_3N](HSO_4)_2$, is formed, which is also present in nitrosyl-sulphuric acid.

Isomerism occurs in the salts as well, and Hantzsch suggests that all salts of metals below hydrogen in the electrometric series (p. 151) are non-polar. The effect of this is shown in some of the salts of nitrous acid. Silver nitrite with methyl iodide forms both the methyl ester of nitrous acid (I.) and nitromethane (II.):

I. $\left[N\genfrac{}{}{0pt}{}{O}{O\,.\,CH_3} \right]$.   II. $\left[O_2 : N \right] CH_3$.

The CH_3 group is only connected directly with an oxygen atom in the esters and is connected through this to the nitrogen atom, while in the nitro-compounds its relations to the central nitrogen atom are dominant. On reduction, the nitro-compounds pass into amino-compounds in which the carbon and nitrogen are still adjacent, while the esters are saponified by the treatment and the nitrogen and carbon are thus separated. In silver nitrite the two isomers exist side by side:

I. $\left[N\genfrac{}{}{0pt}{}{O}{OAg} \right]$.   II. $\left[N(O)_2 \right] Ag$.

In complex compounds it is possible to isolate both isomers, as they are differently coloured. The following manner of writing them explains that in the pale yellow coloured compounds, corresponding to the silver salt I., the cobalt atom is joined to nitrogen with the help of oxygen, while in the brick-red ones corresponding to the silver salt II., the union does not proceed by way of oxygen.[1]

Chamois coloured	I.	$\left[Co\genfrac{}{}{0pt}{}{(ONO)_2}{en_2} \right] X$		$\left[Co\genfrac{}{}{0pt}{}{(ONO)_2}{(NH_3)_2}{(C_6H_5N)_2} \right] X.$	
Brick red	II.	$\left[Co\genfrac{}{}{0pt}{}{(NO_2)_2}{en_2} \right] X$		$\left[Co\genfrac{}{}{0pt}{}{(NO_2)_2}{(NH_3)_2}{(C_6H_5N)_2} \right] X.$	
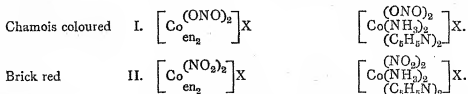
[1] Werner, *Ber.*, 1907, 40, 768.

Whereas nitrous acid is a weak acid, nitric acid, as is known from conductivity determinations, the inversion of cane sugar, and from its rate of saponifying esters, is among the strongest of acids.

✓ *Oxidising Action.*—The oxidising action of nitric and nitrous acids is one of their most characteristic properties. Measurements of potential (*cf.* p. 164) show that nitric acid is the stronger of the two oxidising media, but nitrous acid acts more rapidly. The rapid oxidising action is always due to the NO_2, which is formed as an intermediate product; this is evolved more quickly from HNO_2 than from HNO_3, in which NO_2 and O are formed by way of the anhydride N_2O_5. Nitric acid treated with platinum black oxidises substances more quickly than if this were not present, and even decomposes by itself into NO_2, O and H_2O.

Oxidation by NO_2 is so much more rapid than by HNO_3 that in practice only the NO_2 formed from the nitric acid acts as the oxidising agent. Colourless nitric acid has either very little or no oxidising effect on sulphur, metals, etc. If, however, a very little NO_2 is introduced oxidation immediately occurs. The nitric acid is thereby reduced, still more NO_2 is formed, and the rate of oxidation increases with the rising concentration. For this reason nitric acid, which has ✓ previously been saturated with NO_2 (red or **fuming nitric acid**), is an oxidising agent which is specially rapid in its action. This fuming nitric acid is obtained either by passing nitrogen dioxide, which has been separately prepared, into the colourless acid, or by partial reduction of the nitric acid with formaldehyde, or by distillation of a nitrate with the actual quantity of sulphuric acid theoretically required. The high temperature necessary for carrying out the complete reaction (*cf.* pp. 669-70) causes sufficient decomposition of the nitric acid.

The red fuming acid has a higher specific gravity than the colourless acid, viz.:

Per cent. NO_2 added	.	.	2·9	7·5	12·7
Density	.	.	.	1·507	1·526	1·544

If the NO_2 formed in the reduction of the nitric acid is constantly removed the oxidising action almost ceases. The removal may be effected, *e.g.* by adding some urea, which reacts with the nitrous acid or N_2O_3 formed from the NO_2, with the formation of nitrogen, carbon dioxide and water:

$$H_2 \; N{-}{-}CO{-}{-}N \; H_2$$
$$O{=}{=}N{-}{-} \; O \; {-}{-}N{=}{=}O$$
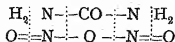
Nitric acid mixed with urea does not oxidise organic substances, but only nitrates them; many nitrations can be carried out only in the presence of urea. The mixture, moreover, does not dissolve

copper. The urea in this case acts as a "negative catalyst," *i.e.* it inhibits the reaction which gives the "positive catalyst," NO_2. This by-product favours the reaction which has led to its formation; decomposition promotes further decomposition (autocatalysis).

Concentrated nitric acid, in general, oxidises the elements to compounds of at least the same oxygen content as those formed on burning them in oxygen. Thus metals form oxides, which then yield nitrates with the excess of nitric acid. If the oxides are not soluble in the acid they are formed as such, *e.g.*:

$$Sn \longrightarrow SnO_2, \quad Sb \longrightarrow Sb_2O_5, \quad Mo \longrightarrow MoO_3, \quad W \longrightarrow WO_3.$$
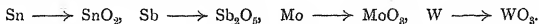
Noble metals (gold, platinum, iridium) are generally not attacked. Some baser metals, even when they come after hydrogen in the electrometric series, are converted into nitrates, since their affinity for oxygen has to be considered, and not the electric potential.

Non-metals are often oxidised to a higher stage than when burnt in oxygen. Thus, sulphur gives not only SO_2 but SO_3 and sulphuric acid, arsenic gives not arsenious but arsenic acid, iodine forms iodic acid. Selenium, however, gives selenious and not selenic acid. Where combustion in oxygen yields the highest oxide this is also obtained on oxidation with nitric acid. Thus carbon and boron form carbonic and boric acids; phosphorus yields phosphoric acid, although here the trioxide (phosphorous acid) is formed as an intermediate product which may be isolated as in the combustion. These reactions are often only complete on warming. Hydrogen and ammonia are also oxidised by nitric acid, but only on heating, or in the presence of platinum black, when flame is produced.

The reduction products of the non-metals naturally react even more readily than the elements themselves. HI is instantaneously oxidised to iodine, H_2S even explodes with nitric acid; this explosion is prevented if NO_2 is entirely excluded.

The oxidation and reduction series (p. 164) gives information about the oxidising power of the nitrogen acids towards reducing ions. From this it is noticeable that the oxidising effect surpasses that of hypochlorite and dichromate, and that, *e.g.*, ferrous ions, arsenious acid and stannous salts, and the stronger reducing media in addition, are easily oxidised. The oxidation of hydrochloric acid in *aqua regia* leads to the formation of NO, Cl_2, and NOCl (p. 682). Nitrous acid is a somewhat weaker oxidant than nitric acid, and it is only able to oxidise solutions of SO_2 more rapidly than HNO_3 because this is a time and not an intensity phenomenon. It is also oxidised to nitric acid by media of oxidising power greater than that of nitric acid; the dioxides of lead and manganese, hydrogen peroxide and permanganic and chloric acids are of practical value here. On the other hand, the stronger reducing agents ($SnCl_2$, H_2S, HI, sodium amalgam) act on it in the same way

as on nitric acid. The salts of the noble metals ($AuCl_3$, $HgNO_3$) are reduced to the metal by nitrites. The reduction products of both acids are similar, and according to the experimental conditions comprise lower oxides of nitrogen, hyponitrous acid, nitrogen, hydroxylamine and ammonia.

Nitrites.—Since nitrous acid is a fairly weak acid, its salts tend to be hydrolysed. For this reason only salts of the stronger bases are known—those of the alkalis and the alkaline earths—and a few which are distinguished by their small solubility, such as those of univalent mercury, and especially of silver. The nitrites of bases of moderate strength, in particular those of the bivalent heavy metals, are very little known in the neutral condition, but some, such as those of zinc and cadmium, have been described. The tervalent metals, iron, chromium and aluminium, do not give stable nitrites.

The solution of the pure acid is seldom used in the preparation of nitrites. Mercurous nitrite alone is best obtained from mercury and dilute nitric acid containing NO_2, which reacts with the metal and is continually regenerated by the simultaneous reduction of the nitric acid.[1] Nitrites are often obtained by decomposing barium or silver nitrite with the sulphate or chloride respectively of the metal:

$$CaCl_2 + 2AgNO_2 \longrightarrow Ca(NO_2)_2 + 2AgCl,$$
$$MgSO_4 + Ba(NO_2)_2 \longrightarrow Mg(NO_2)_2 + BaSO_4.$$
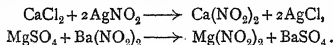
The double decomposition between barium chloride and sodium nitrite may be employed for the preparation of the important barium nitrite in the pure state, provided an excess of sodium nitrite is used. The NaCl formed in the decomposition is sparingly soluble in a $NaNO_2$ solution; the separation of barium nitrite from the excess of sodium nitrite is easily accomplished by reason of the sparing solubility of the barium compound in presence of the common nitrite ion.[2]

The property of nitrates of the alkalis and of barium of decomposing to nitrites on being heated is applied to their preparation: $2NaNO_3 \longrightarrow 2NaNO_2 + O_2$. This decomposition is sometimes assisted by the addition of reducing agents (p. 685); barium nitrite thus prepared contains a considerable amount of oxide, since the decomposition proceeds further than the nitrite stage.

The nitrites of metals with colourless ions are all somewhat yellowish in colour. Silver nitrite, which appears white in the fine form in which it is obtained by precipitation from solution, is yellow when prepared in large crystals. Mercurous nitrite is sulphur yellow. This intense colour of the nitrites of the noble metals as contrasted with the alkali nitrites is in good agreement with a difference in constitution; the alkali nitrites are strong electrolytes, but those of the noble

[1] Rây, *J. Chem. Soc.*, 1905, 87, 172.
[2] Witt and Ludwig, *Ber.*, 1903, 36, 4384.

metals do not dissociate. The latter are probably derived from the neutral and the former from the true acid form of nitrous acid (*cf.* p. 689 for another example of the appearance of both forms of one salt). Most nitrites melt on heating, those of the alkalis to yellow liquids which decompose at higher temperatures. The more noble the metal the lower the decomposition temperature; the alkali nitrites decompose slowly at red heat, barium nitrite decomposes at about 220°, silver nitrite at 140°, mercury nitrite at 75°, gold nitrite is very unstable, even at room temperature. On boiling with water decomposition also sets in, since nitrous acid is formed by hydrolysis. A basic salt remains, as well as some nitrate which is formed by the action of NO_2 on the base which is formed. For this reason the nitrites of the heavy metals cannot be isolated in the pure condition by evaporation of their aqueous solutions. In the noble metals the decomposition in aqueous solution is accompanied by deposition of the metal, since here the lower oxides of nitrogen exert their reducing power. Thus the nitrites of uni- and bi-valent mercury decompose on contact with water free from nitric acid, and even when left in damp air NO_2 is evolved and a corresponding quantity of nitrate is simultaneously formed; silver nitrite solution decomposes at just above room temperature and more quickly on boiling: $2AgNO_2 \longrightarrow Ag + NO + AgNO_3$. This decomposition, if the NO is not allowed to escape, leads to a condition of equilibrium, which, according to Abegg and Pick,[1] may be expressed thus: $Ag^{\cdot} + 2NO_2' \rightleftharpoons NO + NO_3' + Ag$.

The nitrites have no marked ability to form crystals, though they are not amorphous. Only the noble metal nitrites give large crystals—silver nitrite in particular crystallises in long thin needles. The alkali nitrites form only very small crystals. All nitrites, with the exception of silver nitrite, are hygroscopic, many are even deliquescent. Sodium nitrite is markedly less hygroscopic than potassium nitrite. All except silver and mercurous nitrites are easily soluble in water. Thus at room temperature 1 part of water dissolves 0.8 part $Ba(NO_2)_2$, 1 part $NaNO_2$ or 3 parts KNO_2, but only 0.003 part $AgNO_2$. The nitrites are low in water of crystallisation; those of the alkalis and the noble metals are generally anhydrous; those of the alkaline earths contain 1 mol., and $Mg(NO_2)_2$ somewhat more water. The basic salts have as yet been little investigated; they resemble the basic nitrates (*cf.* p. 698) in their structure.

The complex nitrites are more stable to water, those of the less noble metals being obtainable in crystalline form, and the stability of the complex varies considerably as in the complex chlorides. Besides the weak complexes known as "double nitrites," corresponding to the double chlorides, very stable complexes are known—the nitrito-salts corresponding to the "chloro-salts." To the weak complexes belong,

[1] *Z. anorg. Chem.*, 1905, 51, 1.

e.g. the easily decomposed compounds: $Cs[Ag(NO_2)_2]$, $Cs_2[Ca(NO_2)_4]$, $K_2[Pb(NO_2)_4]$, and the following "triple salts," which it is curious to find in this class:

$$PbK_2[M(NO_2)_6] \qquad (M = Fe, Cu, Co, Ni) \qquad BaK_2[Ni(NO_2)_6],$$

together with the difficultly soluble salt $5Bi(NO_3)_3$, $9CsNO_2$, $6NaNO_2$, which is approximately $Cs_2Na[Bi(NO_2)_6]$ and serves for the quantitative estimation of sodium or bismuth.

Of the strong complexes the best known is potassium cobaltinitrite, $K_3[Co(NO_2)_6]$, which is isomorphous with the corresponding but less deeply coloured compounds of Rh and Ir; $Na_3[Co(NO_2)_6]$ is used for the precipitation of cobalt or potassium with formation of $K_2Na[Co(NO_2)_6]H_2O$ under suitable conditions.[1]

Many other nitrito-salts of cobalt, chromium and platinum have already been described on p. 312 *et seq.*

Of the ammines of the bivalent metals, the nickel compound, $Ni(NO_2)_2 \cdot 4NH_3$, is distinguished by its beautiful red colour; but the addition of ammonia to the nitrites of the other bivalent metals is not very readily carried out.

Ammonium nitrite, NH_4NO_2, occupies a separate position among the nitrites in many respects. This white hygroscopic compound, which may be synthesised from its elements and which occurs in the atmosphere, is easily formed as white needles when a mixture of air and ammonia is passed over platinised asbestos. However, it very easily decomposes at room temperature, and at higher temperatures is explosive, especially if hydrogen or ammonia is present. In aqueous solution the decomposition is completed quietly and gives pure nitrogen (*cf.* p. 178): $NH_4NO_2 \longrightarrow N_2 + 2H_2O$. If the aqueous solution is shaken it froths like sparkling wine. The velocity of decomposition is appreciably greater if the medium is acidic instead of ammoniacal, although the reaction products are the same. The addition of nitrites and ammonium salts also accelerates the decomposition, while other salts hinder it. Otherwise no catalysts which accelerate its decomposition are known. Investigations by Arndt[2] and by Blanchard[3] show that the hydrogen ions or the free nitrous acid formed on hydrolysis in aqueous solution start the decomposition.

Nitrates.—The salts of nitric acid are almost exclusively obtained by the action of the free acid on metals, oxides or carbonates, or a mixture of nitrogen oxides and air may be used instead of the acid (*cf.* p. 674). The important formation of nitrates in nature takes place with the aid of nitrifying bacteria (p. 684). Since nitric acid is a strong acid, these salts may be obtained undecomposed and crystalline by evaporating their aqueous solutions; only for the salts of very weak

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[1] Cumbers and Coppock, *J. Soc. Chem. Ind.*, 1937, 56, 405 T.
[2] *Z. physikal. Chem.*, 1902, 39, 64.   [3] *Ibid.*, 1902, 41, 681.

bases is the addition of some nitric acid in excess desirable in order to repress hydrolysis. Weak bases form nitrates less readily than chlorides; thus quadrivalent tin, lead, manganese, etc., give chlorides, but no nitrates, and in the same way but little is definitely known of arsenic and antimony nitrates. The nitrates of lower stages of oxidation are not always obtainable, *e.g.* cuprous or chromous nitrates cannot be obtained; nitrates of co-ordinated univalent copper are, however, quite stable (see p. 700) and ferrous and mercurous nitrates are easily obtained.

Nitrates nearly all correspond to HNO_3, but Na_3NO_4 (*i.e.* Na_3PO_4 type) has been prepared from Na_2O and $NaNO_3$; it is decomposed by water, but its homogeneity has been established by X-ray analysis.[1] Corresponding salts of orthonitrous acid, *e.g.* Na_3NO_3, have also been prepared.

The nitrate ion exhibits no absorption in the visible spectrum; hence nitrates of metals with colourless ions are colourless, and the colour of coloured ions is not changed on nitrate formation. Ferric nitrate has the pale violet colour of ferric alum and not the brown of the chloride; cupric nitrate is blue like hydrated cupric sulphate and is not like the anhydrous cupric salts.

All known nitrates dissolve easily in water; even that of lead, which forms insoluble salts with almost all inorganic acids. The nitrates of some complex ions are least soluble: thus hexamminocobaltic nitrate, $[Co(NH_3)_6](NO_3)_3$, dissolves only in 60 parts of water at room temperature, and the purpureo-nitrate, $[Co(NH_3)_5Cl](NO_3)_2$, and others are also fairly difficultly soluble. The least soluble of all nitrates, which may be used for the quantitative precipitation of nitric acid, is that of an organic base:

$$C_6H_5 \cdot N \text{———} N$$

which is called "Nitron" owing to the insolubility of its nitrate.

The solubility of nitrates is much greater in hot than in cold water, a property which is used to obtain potassium nitrate from sodium nitrate. If the latter is decomposed by the requisite quantity of potassium chloride, the free ions of the four salts, NaCl, KCl, $NaNO_3$ and KNO_3, are formed in solution. Of these, NaCl is least soluble on heating, while, in the cold, KNO_3 has the smallest solubility. If now KCl is decomposed with hot $NaNO_3$, NaCl separates out, and after this has been filtered off, KNO_3 crystallises on cooling. The two salts,

[1] Zintl, Morawietz and Woltersdorf, *Naturwiss.*, 1935, **23**, 197; Zintl and Haucke, *Z. physikal. Chem.*, 1935, **174**, 312.

e.g. the easily decomposed compounds: $Cs[Ag(NO_2)_2]$, $Cs_2[Ca(NO_2)_4]$,
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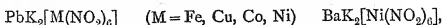
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Many other nitrito-salts of cobalt, chromium and platinum have
already been described on p. 312 *et seq.*

Of the ammines of the bivalent metals, the nickel compound,
$Ni(NO_2)_2 \cdot 4NH_3$, is distinguished by its beautiful red colour; but
the addition of ammonia to the nitrites of the other bivalent metals
is not very readily carried out.

Ammonium nitrite, NH_4NO_2, occupies a separate position among
the nitrites in many respects. This white hygroscopic compound,
which may be synthesised from its elements and which occurs in the
atmosphere, is easily formed as white needles when a mixture of air
and ammonia is passed over platinised asbestos. However, it very
easily decomposes at room temperature, and at higher temperatures is
explosive, especially if hydrogen or ammonia is present. In aqueous
solution the decomposition is completed quietly and gives pure nitrogen
(*cf.* p. 178): $NH_4NO_2 \longrightarrow N_2 + 2H_2O$. If the aqueous solution is
shaken it froths like sparkling wine. The velocity of decomposition is
appreciably greater if the medium is acidic instead of ammoniacal,
although the reaction products are the same. The addition of nitrites
and ammonium salts also accelerates the decomposition, while other salts
hinder it. Otherwise no catalysts which accelerate its decomposition
are known. Investigations by Arndt[2] and by Blanchard[3] show that
the hydrogen ions or the free nitrous acid formed on hydrolysis in
aqueous solution start the decomposition.

Nitrates.—The salts of nitric acid are almost exclusively obtained
by the action of the free acid on metals, oxides or carbonates, or a
mixture of nitrogen oxides and air may be used instead of the acid
(*cf.* p. 674). The important formation of nitrates in nature takes place
with the aid of nitrifying bacteria (p. 684). Since nitric acid is a
strong acid, these salts may be obtained undecomposed and crystalline
by evaporating their aqueous solutions; only for the salts of very weak

[1] Cumbers and Coppock, *J. Soc. Chem. Ind.*, 1937, 56, 405 T.
[2] *Z. physikal. Chem.*, 1902, 39, 64.   [3] *Ibid.*, 1902, 41, 681.

bases is the addition of some nitric acid in excess desirable in order to repress hydrolysis. Weak bases form nitrates less readily than chlorides; thus quadrivalent tin, lead, manganese, etc., give chlorides, but no nitrates, and in the same way but little is definitely known of arsenic and antimony nitrates. The nitrates of lower stages of oxidation are not always obtainable, *e.g.* cuprous or chromous nitrates cannot be obtained; nitrates of co-ordinated univalent copper are, however, quite stable (see p. 700) and ferrous and mercurous nitrates are easily obtained.

Nitrates nearly all correspond to HNO_3, but Na_3NO_4 (*i.e.* Na_3PO_4 type) has been prepared from Na_2O and $NaNO_3$; it is decomposed by water, but its homogeneity has been established by X-ray analysis.[1] Corresponding salts of orthonitrous acid, *e.g.* Na_3NO_3, have also been prepared.

The nitrate ion exhibits no absorption in the visible spectrum; hence nitrates of metals with colourless ions are colourless, and the colour of coloured ions is not changed on nitrate formation. Ferric nitrate has the pale violet colour of ferric alum and not the brown of the chloride; cupric nitrate is blue like hydrated cupric sulphate and is not like the anhydrous cupric salts.

All known nitrates dissolve easily in water; even that of lead, which forms insoluble salts with almost all inorganic acids. The nitrates of some complex ions are least soluble: thus hexamminocobaltic nitrate, $[Co(NH_3)_6](NO_3)_3$, dissolves only in 60 parts of water at room temperature, and the purpureo-nitrate, $[Co(NH_3)_5Cl](NO_3)_2$, and others are also fairly difficultly soluble. The least soluble of all nitrates, which may be used for the quantitative precipitation of nitric acid, is that of an organic base:

$$C_6H_5 \cdot N \underline{\hspace{2cm}} N$$
$$\begin{array}{c} N \cdot C_6H_5 \\ HC \diagup \diagdown C \\ N \cdot C_6H_5 \end{array}$$

which is called "Nitron" owing to the insolubility of its nitrate.

The solubility of nitrates is much greater in hot than in cold water, a property which is used to obtain potassium nitrate from sodium nitrate. If the latter is decomposed by the requisite quantity of potassium chloride, the free ions of the four salts, $NaCl$, KCl, $NaNO_3$ and KNO_3, are formed in solution. Of these, $NaCl$ is least soluble on heating, while, in the cold, KNO_3 has the smallest solubility. If now KCl is decomposed with hot $NaNO_3$, $NaCl$ separates out, and after this has been filtered off, KNO_3 crystallises on cooling. The two salts,

[1] Zintl, Morawietz and Woltersdorf, *Naturwiss.*, 1935, **23**, 197 ; Zintl and Haucke, *Z. physikal. Chem.*, 1935, **174**, 312.

$NaNO_3$ and KCl, do not both appear in the solid condition, since their solubility is intermediate between that of NaCl and KNO_3 at the temperatures employed.

The considerable rise in the solubility of potassium nitrate with temperature may be seen from the following figures.   100 g. of water dissolves :

At	.	. 0°	10°	21.5°	30.2°	40.1°	50.0°	59.2°	68.3°
g. KNO_3	.	13.3	20.8	33.5	46.2	64.1	85.4	107.7	132

The solubility curve of sodium nitrate is much flatter ; it begins higher, crosses that of potassium nitrate at about 68° and then proceeds below it.   100 g. water dissolves :

At	.	.	.	0°	20°	50°	80°	110°
g. $NaNO_3$	.	.		72.9	87.5	112	148	200

Ammonium nitrate is the most soluble nitrate ; at the ordinary temperature it requires only about half its weight of water for solution.   Rubidium nitrate is more soluble and caesium nitrate almost as soluble as potassium nitrate, if the calculations are made in grams ; if expressed in gram molecules these salts are less soluble than the potassium salt.   Of the more important nitrates, silver nitrate dissolves in 100 g. of water as follows :

At .	.	.	.	. 0°	50°	100°	133°
g. $AgNO_3$	.	.	.	115	400	910	1941

and 100 parts of lead nitrate solution contain :

At	.	.	.	0°	50°	100°
Parts $Pb(NO_3)_2$		.		26.7	44.0	56.0

The nitrates of bismuth and mercury do not dissolve without decomposition, but yield basic salts.

Many nitrates are hygroscopic; this property is not possessed by the potassium salt (in contrast to that of sodium), and it is therefore more suitable for many technical purposes (preparation of gunpowder, fireworks).   Barium, lead and silver nitrates are not hygroscopic.

The water of crystallisation contained in the solid nitrates is comparable to that of the chlorides.   The alkali nitrates are anhydrous, though lithium nitrate contains some water ; in the alkaline earths the tendency to combine with water of crystallisation increases from barium to magnesium, so that while the former is anhydrous at room temperature, strontium and calcium nitrates contain 4, and magnesium nitrate 6 mols. H_2O, the latter taking up even 9 mols. in the cold.   Most other nitrates of bivalent metals have 6 mols. of water at room, and 9 mols. at lower temperatures, e.g. those of nickel, cobalt, copper, manganese and zinc; cadmium nitrate contains only 4, and bismuth nitrate 5 mols. H_2O, although $Cd(NO_3)_2$ forms a nonahydrate at low temperatures; the tervalent metals (Fe, Al, Cr) form nonahydrates at room temperature.   All the non-hygroscopic nitrates are anhydrous, including those of silver and lead.   Some of the nitrates of the bivalent

metals may be dehydrated almost without decomposition, but those of tervalent metals lose almost all their nitric acid and are converted into oxides. The phenomena are similar to those described in the dehydration of chlorides (p. 272), although the loss of acid from nitrates is a little greater.

Many nitrates melt on dry heating and then undergo decomposition. This decomposition may result in the formation of nitrite, oxide or the free metal:

$$2KNO_3 \longrightarrow 2KNO_2 + O_2 \qquad 2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$$
$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2.$$
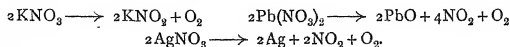
Oxide formation occurs in the less positive, and metal formation in the noblest metals, the oxides of which are already unstable at the decomposition temperature of the nitrates. Even when nitrites are formed, nitrogen and its oxides appear as by-products and potassium and sodium nitrates on strong heating give these secondary products, but the first portion of the gas which is evolved is pure oxygen.

This liberation of oxygen makes the molten nitrates strong oxidising agents. The oxidising effect is almost the same as that of concentrated nitric acid (p. 690), but can proceed more rapidly, since it is carried out at higher temperatures, and it may almost amount to explosion. Best known is the action of saltpetre on carbon and sulphur (gunpowder), which when started locally by heating (percussion cap) proceeds rapidly by itself; it can always take place without explosion if the gases formed are given a free passage, while in an enclosed space it leads to explosion, through the pressure and percussion effect due to the heat of reaction, which automatically increase with the quantity of gas evolved. The evolution of oxygen from nitrates is an endothermic process; it therefore only proceeds by itself if the oxygen takes part in a process evolving more heat than is required to decompose the nitrate. This occurs in the firing of black powder by the formation of SO_2 and CO_2. The conditions are specially favourable if portions of the nitrate molecule itself react with the oxygen which is to be split off with production of heat. This occurs in ammonium nitrate, NH_4NO_3, in which the ammonia can be burnt by the nitrate oxygen, so that the decomposition of this nitrate proceeds exothermally. Ammonium nitrate is therefore used to a large extent as an explosive, and, if it is mixed with oxidisable substances (since its oxygen content is greater than can be utilised by the hydrogen present) may give violent explosions. The simple decomposition into N_2O and H_2O on heating cautiously has already been discussed on p. 667. It is decomposed thus below 200°, but with extremely careful heating a great part of it may be split up, undecomposed, into NH_3 and HNO_3, when it shows the phenomenon of sublimation by condensing again on

cooler portions of the vessel. The sublimation is very successful if carried out under reduced pressure, and under 11 mm. the molten nitrate boils almost undecomposed at 100°.

The melting points of some nitrates, fusible without decomposition, are:

	NH_4NO_3	$LiNO_3$	$NaNO_3$	KNO_3	$CsNO_3$	$Ba(NO_3)_2$
M.pt.	170°	264°	314°	339°	414°	592°

If several of these nitrates are mixed the melting point is depressed; mixtures of nitrates are used for thermostat baths for moderate temperatures, as they are a fairly cheap filling material. A mixture of equimolecular quantities of $NaNO_3$ and KNO_3, which melts at 218°, is often used. An equimolecular mixture of KNO_3 and $LiNO_3$ melts at 132°.

Some nitrates form numerous modifications in the solid state. In this respect ammonium nitrate especially has been studied. The transition points have been determined by optical and thermometric methods, by measurement of volume, expansion, solubility, etc., and the influence of pressure on the displacement of these points has also been studied. No less than five different solid forms of this salt have been found: a tetragonal form is converted to a rhombic at $-17°$, which changes to another rhombic form at 32·1°. This again at 84·7° goes into a monoclinic form, and the last changes at 125·2° into a regular form. All the changes are reversible.[1]

Basic and Complex Nitrates.—The hydrated nitrates of bivalent metals, if they cannot be dehydrated without decomposition, give, on heating, basic salts, to which the formulae $M(NO_3)_2$, $2MO$, aq. or $M(NO_3)_2$, $3MO$, aq. are given. Werner[2] assumes that metal hydroxide molecules are formed in the decomposition, which link up as neutral bidentate chelate groups with the metal atom. Typical basic nitrates can thus be formulated:

i.e. $Mg(NO_3)_2$, $2MgO$, aq.　　　$Zn(NO_3)_2$, $3ZnO$, aq.　　　$Cu(NO_3)_2$, $3CuO$, aq.
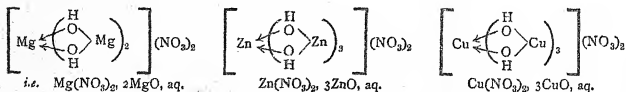
The anhydrous basic mercury nitrate would correspond to these:

$$[Hg(OHg)_2](NO_3)_2, \qquad i.e. \ Hg(NO_3)_2, \ 2HgO.$$

Ammines of the nitrates, in which ammonia replaces some or all of the water of crystallisation, are quite stable. In their stability they correspond roughly to the ammines of the chlorides, and have the same colours. Many are obtained when the anhydrous nitrates are acted upon by

[1] Early and Lowry, *J. Chem. Soc.*, 1919, 115, 1387.
[2] *Ber.*, 1907, 40, 4444.

gaseous ammonia, others when ammonia is passed into their concentrated solutions. The nitrates of the alkalis, which yield no hydrates, do not form ammines. Ammonium nitrate has a special tendency to take up ammonia, when it liquefies without forming an ammine, and gives "Divers's liquid," described on p. 622.

Nitrates do not easily form complex compounds in which several NO_3 groups co-ordinate with a metal atom. The number of easily dissociated nitrato-salts, the so-called double nitrates, is not comparable with that of the double halides or sulphates. Almost the only metals which can act as central atoms in double nitrates are those with high atomic weights, in particular Ba, Hg, Au, Tl, Pb, Th and Bi. The formula of potassium barium nitrate, $K_2[Ba(NO_3)_4]$, serves as an example of the constitution of these compounds.

Bismuth and the metals of the rare earths, on the other hand, give rise to a remarkable class of double nitrates, which are important for the isolation of these metals because they crystallise readily; their constitution recalls that of the alums. They correspond to the formulae :

$$M_3^{II}[M^{III}(NO_3)_6]_2, 24H_2O, \quad i.e. \quad 2M^{III}(NO_3)_3, 3M^{II}(NO_3)_2, 24H_2O.$$
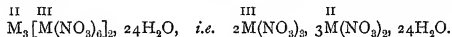
Mg, Zn, Mn, Co, Ni and others are the bivalent metal in these complexes.

Hydrogen can also occasionally act as a central atom, and then the so-called acid nitrates (nitrato-acids) result, of which those of the alkali metals of high atomic volume are known, e.g.: KNO_3, HNO_3, and KNO_3, $2HNO_3$, and the corresponding compounds of rubidium, caesium and ammonium.[1] These compounds correspond exactly, in their structure, behaviour and properties, to the acid halides (p. 234). For the greater part they are stable only at low temperatures, but are well characterised and crystallise from a strong nitric acid solution of the nitrates. Aurinitrato-acid is related to them: $Au(NO_3)_3$, HNO_3, i.e. $H[Au(NO_3)_4]$. The most stable compounds, however, are those with cations of even greater volume than those of the alkalis, e.g.:

$$[Co(NH_3)_6](NO_3)_3 . HNO_3,$$

$$\left[Co_{H_2O}^{(NH_3)_5}\right](NO_3)_3 . HNO_3, \qquad \left[Cr_{(H_2O)_2}^{(NH_3)_4}\right](NO_3)_3 . HNO_3.$$
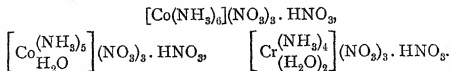
In these complex nitrates the metals can often exhibit higher valencies than usual (cf. cobaltammines, pp. 300-1). The compound of bivalent silver, $[Ag^{II}(C_5H_5N)_4](NO_3)_2$, is an example of this, and is formed at the anode when a pyridine solution of silver nitrate is electrolysed. The orange-red crystals are isomorphous with those of the bivalent copper compound.[2] The silver compound is at once decolorised on addition of H_2O_2, and with $MnSO_4$ permanganate is

[1] Groschuff, Ber., 1904, 37, 1486.   [2] Barbieri, ibid., 1927, 60, 2424

formed. A similar example may be noted in the silver persulphate compound $Ag^{II}S_2O_8,4C_5H_5N$, while the complexes containing o-phenanthroline and o-dipyridyl are so stable that the chlorate, perchlorate, nitrate and sulphate of bivalent silver can be obtained by double decomposition.[1] Barbieri[2] has prepared argentic picolinate
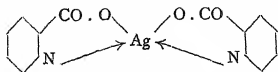
by electrolytic oxidation of the Ag^I salt; it is isomorphous with cupric picolinate. These compounds of bivalent silver are paramagnetic. Of simpler bivalent silver compounds, AgF_2 is well established[3]; it is obtained by the action of fluorine on silver at room temperature. It is relatively stable and gives ozone with water.

On the other hand, in complex nitrates of copper the univalent condition is stabilised, ethylene-thiourea cuprous nitrate
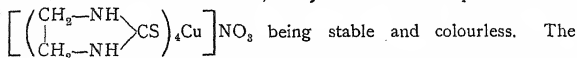
 being stable and colourless. The analogous sulphate, $[(C_3H_6N_2S)_3Cu]_3SO_4$ is also stable. Acetonitrile, succinonitrile, or thiourea likewise serve to stabilise the univalent varieties.[4]

Analogy with Chlorates.—A discussion of the nitrates cannot be concluded without referring to their similarity to the chlorates. An essential reason for this may lie in similarity in form between the radicals $-ClO_3$ and $-NO_3$. This produces a similar spatial arrangement in the salts, so that chlorates and nitrates are isomorphous; a nitrate radical may be replaced by a chlorate radical and *vice versa* without disturbing the symmetry, the spatial relationships and the direction of the crystallisation forces. This similarity is also exhibited in many other properties: the solubility relationships in both classes of salts are comparable throughout: the salts with the largest cations (alkalis, complexes) are the least soluble, those of multivalent metals, which have the smallest atomic volumes, the most soluble. Even the power of adding on water of crystallisation and ammonia is parallel throughout both classes, as is the small tendency to form auto-complexes. It is mainly the "physical" properties of both classes of salts, and those chemical ones which are most obvious through the physical properties, which are comparable. Recent work of Pauling indicates a fundamental similarity in electronic structure.

Hyponitrous Acid, $(HNO)_2$.—Hyponitrous acid is always obtained from its salts, the hyponitrites. These are produced if an opportunity is given for the formation in alkaline solution of the radical $=N.OH$, which immediately polymerises to the bimolecular form. The formation of $HO.N=$ takes place either by the reduction of NO (nitric oxide) or of $HONO$ (nitrous acid), by the oxidation of $HONH_2$ (hydroxylamine), or by the decomposition of many hydroxylamine derivatives.

[1] Hieber and Mühlbauer, *ibid.*, 1928, **61**, 2149; Morgan and Burstall, *J. Chem. Soc.*, 1930, 2594; Barbieri, *Atti R. Accad. Lincei*, 1932, vi., **16**, 44.
[2] *Atti R. Accad. Lincei*, 1933, vi., **17**, 1081.   [3] Jockusch, *Naturwiss.*, 1934, **22**, 561.
[4] Morgan and Burstall, *J. Chem. Soc.*, 1928, 143.

The reduction of NO or HNO_2 to $HO.N=$ is best accomplished with the aid of sodium amalgam, and Partington and Shah[1] consider that this is the best method of preparation; stannites, ferrous hydroxide or electrolytic reduction with a mercury cathode also yield $=NOH$. The NO may either be passed into the solution or used in the form of its addition product with sulphite, the salt of nitrososulphurous acid.

Hydroxylamine may be oxidised by means of the oxides of noble metals, or by nitrous acid :

$$HON \; \underline{H_2+O} \; Hg \xrightarrow{-H_2O} HON =, \quad HON \; \underline{H_2+O} \; NOH \xrightarrow{-H_2O} HON = NOH.$$
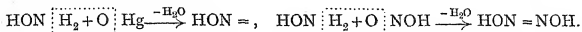
The desired result is also obtained by eliminating sulphurous acid from the hydroxylamine sulphonic acid molecule by means of alkali, which is a convenient method of preparing hyponitrites :

$$HON \; \underline{H.SO_3H} \; \xrightarrow{-H_2SO_3} HON =.$$
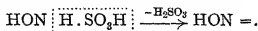
Interaction of nitric oxide and atomic hydrogen at the temperature of liquid air yields a mixture of hyponitrous acid and nitramide.[2]

On passing NO into solutions of metals in liquid ammonia combination ensues :

$$2Na + 2NO \longrightarrow (NaON)_2,$$

but the gelatinous products are not identical with the hyponitrites[3]; they are probably monomeric $\overset{+}{Na}[N\!\!=\!\!O]^-$ *i.e.* $\overset{+}{Na}[N^4\!\!\equiv\!\!O^4]$. A similar reaction occurs if the addition compound of sodium and pyridine is similarly treated :

$$2Na(py)_2 + 2NO \longrightarrow (NaON)_2 + 4py.$$

Direct molecular weight determinations on free hyponitrous acid show that it is bimolecular; it is easily soluble in water as well as in many organic solvents. This molecular weight is also confirmed by those of the esters. The existence of some acid salts is of less importance as evidence. The acid ammonium salt is obtained by passing ammonia into an ethereal solution of the acid; but in this way almost all monobasic organic acids give similar "acid" ammonium salts. The acid salts of metals are not known, and only in the alkaline earths are there indications of their existence.

It is generally accepted that the union of the two $HON=$ radicals takes place through the free nitrogen valencies. Hyponitrous acid then has the formula $HON = NOH$, and as it contains the group $-N = N-$ it is thus an inorganic azo-compound.

The *free acid* is obtained by decomposing the silver salt with ethereal hydrochloric acid and evaporating the ether. It forms white leaflets which easily explode, and also decompose after standing for some time.

[1] *J. Chem. Soc.*, 1931, 2071.   [2] Harteck, *Ber.*, 1933, 66 [B], 423.
[3] Zintl and Harder, *Ber.*, 1933, 66 [B], 760.

It is much more stable in aqueous solution, and is decomposed by sulphuric acid with the elimination of water :

$$H_2N_2O_2 \longrightarrow H_2O + N_2O,$$
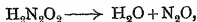
but it cannot be synthesised from N_2O and H_2O. It has no oxidising properties, and even HI is not attacked by it in the pure condition; on the other hand, it may be converted into nitrous or nitric acids by means of strong oxidants ($HMnO_4$). It is reduced to hydrazine with difficulty by nascent hydrogen. Its acidic properties are weak and its aqueous solution conducts electricity with extraordinary difficulty. Nevertheless, only a few heavy metals (Pb) give basic salts, and most of the salts are normal. The bright yellow, dense, flaky, anhydrous silver salt is characteristic and suitable for isolation; it is only a little more soluble than silver chloride, but is dissolved by nitric acid. Even the alkaline earth salts which contain some molecules of water of crystallisation are very slightly soluble, the alkali salts being more easily soluble. The salts can be heated to over 100°; the silver and lead salts explode at a higher temperature.

Nitryl Halides.—These compounds can be regarded as the results of substitution of the hydroxyl groups of nitric acid by halogen atoms. Nitryl chloride, NO_2Cl, is supposed to be formed in various ways, such as by the action of NO_2 on Cl, or of Cl on silver nitrite, but the products have been shown to be mixtures. The pure substance was prepared by the action of ozone on gaseous nitrosyl chloride [1] : $NOCl + O_3 \longrightarrow NO_2Cl + O_2$. At room temperature it is a colourless gas which decomposes at 100° by a unimolecular reaction into NO_2 and Cl, while at 170° the rate of this reaction becomes too great to be measured. The corresponding fluoride, NO_2F, is formed in a different way : $4NO + F_2 \longrightarrow 2NO_2F + N_2$. The properties of these colourless compounds are as follows : NO_2Cl, b.pt. $-15°$ m.pt. $-145°$; NO_2F, b.pt. $-63.5°$, m.pt. $-139°$.

NO_3F is obtained [2] pure and quantitatively at 20° by the interaction of fluorine and anhydrous nitric acid : $HNO_3 + F_2 \longrightarrow NO_3F + HF$. Hydrogen fluoride is removed by anhydrous potassium fluoride, and NO_3F condensed by liquid air ; it boils at $-46°/760$ mm., and melts at $-175°$ (white solid) ; molecular weight (v.d.) agrees with NO_3F. Mechanical shock causes it to explode ; with water it yields nitric acid, hydrogen fluoride, oxygen difluoride and oxygen ; with 2 per cent. NaOH the reaction is $2NO_3F + 2NaOH \longrightarrow 2NaNO_3 + OF_2 + H_2O$. It is to be regarded

as a nitro-derivative of OF_2, viz., $O{=}\!{>}N{-}O{-}F$, in which NO_2 replaces a

fluorine atom.

Hydronitrous Acid (Nitroxylic Acid), H_2NO_2.

—The salts of this interesting acid were isolated by E. Zintl and O. Kohn.[3] In composition it is the hydrate of NO, and as the lowest of the nitrogen oxyacids it is very susceptible to oxidation and readily forms addition compounds.

[1] Schumacher and Sprenger, *Z. Elektrochem.*, 1929, 35, 653 ; *Z. anorg. Chem.*, 1929, 182, 139.

[2] Ruff and Kwasnik, *Z. angew. Chem.*, 1935, 48, 238 ; Yost and Beerbower, *J. Amer. Chem. Soc.*, 1935, 57, 782 ; Cady, *ibid.*, 1934, 56, 2635.   [3] *Ber.*, 1928, 61, 189.

It must be supposed that the tervalent nitrogen in it is not utilising all its three valencies, but has some of the properties of a free radical, as in the metal ketyls:

$$\overset{\displaystyle |}{Na \cdot O \cdot N \cdot O \cdot Na} \qquad\qquad \overset{\displaystyle |}{R_2 = C \cdot O \cdot Na.}$$

Sodium hydronitrite.   Sodium ketyl.
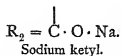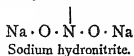
These salts do not give those of higher nitrogen acids by direct oxidation but only addition products.

The alkali salts of hydronitrous acid are obtained by adding sodium nitrite to a solution of the metal in liquid ammonia: $NaNO_2 + Na \longrightarrow Na_2NO_2$. The fine yellow powder which is thus precipitated can be handled only in complete absence of oxygen or moisture. On addition of molecular oxygen the colour changes to brown, with subsequent formation of nitrite and alkali peroxide:

$$2(NaO)_2 = N - + O_2 \longrightarrow (NaO)_2 = N \cdot O \cdot O \cdot N = (ONa)_2 \longrightarrow 2NaNO_2 + Na_2O_2.$$
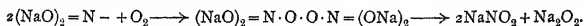
In the same way iodine can be added and then splits off as sodium iodide:

$$(NaO)_2 = N - + I \longrightarrow (NaO)_2 = N \cdot I \longrightarrow NaO \cdot NO + NaI.$$
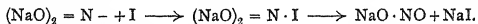
Pyridine gives a red, unstable addition product; water causes a complex decomposition.

Nitrogen Peroxides and the Pernitric (Pernitrous) Acids.— A peroxide of nitrogen seems to be formed by the action of a silent electric discharge on a mixture of NO_2 and O_2, but it decomposes again even at low temperatures. It can be detected only by the change in colour of the mixture and the appearance of characteristic spectral lines. A gaseous compound of formula NO_3 appears to be the first product of the action of oxygen on nitric oxide, but it is only stable for the fraction of a second. The yellow gas, N_2O_7, which is formed if a large excess of oxygen is present, lasts for a somewhat longer period; it breaks down to NO_2 and oxygen on warming or in time in the cold. Both peroxides may be assumed to be addition products of NO_2 and oxygen.[1] An oxide of formula $(N_3O_4)_x$ is also known.

Schwarz and Achenbach[2] prepared pure NO_3 by the interaction of NO_2 (1 volume) and oxygen (20 volumes) at 1 mm. pressure under the influence of a glow discharge. They obtained colourless, solid NO_3 by incorporating a condensing tube, immersed in liquid air, as a part of the discharge tube. NO_3 decomposes slowly above $-142°$ into $NO_2 + O_2$. It is more stable in aqueous solution, but it does not behave as a single acid anhydride; nitrite, nitrate, and oxygen but not H_2O_2 are produced, e.g.

$$2NO_3 + 2NaOH \longrightarrow NaNO_2 + NaNO_3 + H_2O + O_2.$$
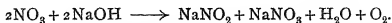
[1] Raschig, *Schwefel- und Stickstoff-studien*, p. 25.
[2] *Ber.*, 1935, 68 [B], 343.

The monomeric formula is based on its low temperature of condensation and its spectrum. Lowry and Lemon[1] also obtained evidence for formation of NO_3 by the action of N_2O_5 and ozone. "Pernitric" acid, to which Raschig[2] gave the formula HNO_4 and which is formed on mixing nitrite solutions with acidified hydrogen peroxide, has been investigated. This mixture is deep yellow and capable of oxidising hydrogen bromide to bromine, which neither nitrous acid nor hydrogen peroxide can do alone. The acid is obtained in the anhydrous condition, according to d'Ans,[3] from 100 per cent. hydrogen peroxide and nitrogen pentoxide as a very unstable and explosive substance, with an intense smell like bleaching powder. Gleu and Harbold[4] reinvestigated Raschig's acid. The conditions of formation are important; sodium nitrite (2 mol.), hydrogen peroxide ($>$2 mol.), much ice and sulphuric acid (1 mol., 2N) are mixed and treated after 2 seconds with excess of NaOH. The excess of H_2O_2, the active oxygen in the peracid, and NO_2' were separately determined; the ratio NO_2' : O was always unity, thus showing the presence of *pernitrite*, HNO_2 . O, *i.e.* HO . O . N : O and absence of pernitrate.

[1] *Nature*, 1935, **135**, 433.   [2] *Ber.*, 1907, **40**, 4585.

[3] *Z. Elektrochem.*, 1911, **17**, 850.

[4] *Z. anorg. Chem.*, 1935, **223**, 305 ; see also Schmidlin and Massini, *Ber.*, 1910, **43**, 1162.

OXYGEN COMPOUNDS OF PHOSPHORUS, ARSENIC, ANTIMONY AND BISMUTH

Trioxides—Tetroxides—Pentoxides—Acids of P, As, Sb, Bi—Hypophosphorous acid —Phosphorous acid—Hypophosphoric acid—Phosphoric acids—Perphosphoric acids—Acids of arsenic and antimony—Bismuthic acid

THE following oxides of P, As, Sb, and Bi are known:

P_4O_6	P_8O_{16}	P_4O_{10}
As_4O_6	Mixt. of As_4O_6 and $(As_4O_{10})_m$	$(As_4O_{10})_m$
Sb_4O_6	$(Sb_4O_8)_m$	$(Sb_4O_{10})_m$
$(Bi_2O_3)_m$	Mixt. of $(Bi_2O_3)_m$ and $(Bi_2O_5)_m$	$(Bi_2O_5)_m(?)$

A peroxide of phosphorus, PO_3, is formed (2 per cent. conversion) when the vapour of P_2O_5, mixed with oxygen, is passed through a heated discharge tube. The blue solid resulting gives a colourless aqueous solution, which may contain $H_4P_2O_8$ and slowly liberates iodine from potassium iodide.[1]

The formulae written without brackets give the molecular size of the oxides in the state of vapour, the bracketed oxides are known only in the solid state and there is no evidence of their molecular complexity. The tetratomic compounds dissociate at a very high temperature, *e.g.* $As_4O_6 \longrightarrow 2As_2O_3$. In the following review they are quoted in this halved form and called, *e.g.* As_2O_3 arsenic trioxide; Sb_2O_4, antimony tetroxide; P_2O_5, phosphorus pentoxide, although diarsenic trioxide, diantimony tetroxide, diphosphorus pentoxide, is a more logical nomenclature. It is, however, not merely accidental that the nuclear atom is fourfold; for the free elements, P, As, Sb and Bi, are also tetratomic in the state of vapour as well as in many of their compounds (*cf.* pp. 114, 738).

The oxides P_8O_{16}, *i.e.* $4P_2O_4$, and Sb_4O_8, *i.e.* $2Sb_2O_4$, are to be considered as compounds of the tri- with the pent-oxide. A polar difference doubtless exists between ter- and quinque-valent phosphorus or antimony.

Sb_2O_4 and P_2O_4 cannot be looked upon as anhydrides of single acids. Although hypophosphoric acid appears to be the hydrate of the tetroxide, $P_2O_4 + 2H_2O$, there exists even less relationship between

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[1] Schenk and co-workers, *Naturwiss.*, 1936, **24**, 651; *Z. anorg. Chem.* 1937, 233, 403.

it and P_2O_4 than between N_2O and $H_2N_2O_2$; the oxide is not formed by dehydration of the acid, nor the acid by hydration of the oxide.

The tri- and pent-oxides, on the other hand, are the anhydrides of the corresponding acids. The acid character is naturally stronger when the atomic weight of the non-metal is smaller, and is thus most pronounced in phosphorus; it is also stronger when the degree of oxidation is higher. In this respect Bi_2O_3 occupies the least favourable position, and the hydrate does not show any acidic characteristics.

The affinity of the element for oxygen also diminishes with rising atomic weight, and with the quantity of oxygen previously present. It is therefore strongest in P_2O_3, which is formed at room temperature from its elements, and weakest in Bi_2O_5, which is converted into Bi_2O_3 and oxygen below 300°. The trioxides are all formed by the direct union of the element with oxygen, while of the pentoxides only that of phosphorus is formed in this way; the others must be prepared by dehydrating the acids.

The Trioxides—*Formation.*—Phosphorus trioxide is formed from phosphorus and oxygen at room temperature, but heating is necessary for the preparation of the other oxides. Rapid formation of phosphorus trioxide takes place only at 60°-100°, and is carried out by passing a rapid stream of air over molten phosphorus in a glass tube, when it burns with a feeble and not very hot flame. The trioxide then volatilises like a mist, which is observed whenever air is allowed to pass over damp phosphorus, *e.g.* in the estimation of oxygen in gas analysis by Hempel's phosphorus pipette. It consists of P_2O_3, the effective component of "phosphorus fumes," which discharge a charged electroscope. For the conditions of its formation *cf.* p. 132. As a consequence of their electric charge the particles are not easily condensed and resemble smokes of NH_4Cl or SO_3. The solid particles remain dispersed through the air as an aerosol. If these smokes are passed through an electric field they are immediately discharged, and the solid is deposited. Arsenic trioxide also tends to form such suspensions ("arsenic fumes"), which condense very slowly; on this account it is necessary to use "poison towers" to catch it when arsenical ores are roasted. The tendency of P_2O_3 to persist in the condition of an aerosol permits of the separation of the pentoxide, which is also formed in the combustion of phosphorus. The fumes are passed through a wad of glass wool, on which the pentoxide is deposited while the trioxide goes farther along the tube.

In the preparation of the other trioxides of this group the simultaneous formation of higher oxides is less pronounced. They are obtained by simply burning the elements in air, or by roasting their sulphides, and the more metallic ones (Sb_2O_3, Bi_2O_3) by hydrolysing the chlorides, sulphates, etc., by the addition of OH' ions, since pure water leads to basic salts which can be hydrolysed further only with

great difficulty. Antimony hydroxide is not formed at all as an intermediate product, while the $Bi(OH)_3$ first formed can be converted to the oxide by heating.

Allotropic Modifications. — All four trioxides appear in different modifications. This is proved with the least certainty in the case of P_2O_3, which is prepared as very voluminous flakes; it is obtained if carefully purified as a transparent crystalline solid, lacking the opaque, waxy appearance of the uncrystallised product.[1] In contrast to this, arsenic, antimony and bismuth trioxides are obtained in both regular and monoclinic (rhombic?) forms, which are especially sharply defined for As_2O_3 and Sb_2O_3. The regular, mainly octahedral or tetrahedral forms are those which are usually obtained under normal conditions. X-ray analysis shows that they consist of double molecules with a diamond type lattice (p. 21) so arranged that each double molecule takes up the position occupied by a carbon atom. The very characteristic brilliant transparent octahedra of As_2O_3 are obtained by rapidly cooling the vapour of white arsenic or by crystallisation from aqueous solution. The monoclinic modification forms very soft, flexible needles. Sb_2O_3 also appears chiefly as octahedra on sublimation and when precipitated from aqueous solution soon changes into octahedra in the mother liquor. The mode of formation of the monoclinic form is not very different from that of the octahedra, since it has nearly the same energy content; *e.g.* the heat of formation of regular Sb_2O_3 is 165·7 Cals., that of the other form 166·9 Cals. Monoclinic As_2O_3 may also be obtained from solution, instead of the octahedral form, when certain foreign substances are present. The forms are scarcely interconvertible below the temperature of vaporisation, but if the monoclinic form is vaporised the octahedral form may be obtained from the vapours. On the other hand, octahedral As_2O_3 is converted into the monoclinic if it is heated at 250° under pressure. No definite transition points have been found, but below about 250° the monoclinic form is the more stable. A sharp transition point for Bi_2O_3 at 704° has been confirmed, but the structure of the form stable at high temperatures is not known.

A third, glassy form of As_2O_3 has been described. This is formed in the commercial sublimation of arsenic by slowly cooling the vapour at temperatures where both the other modifications have almost the same stability. The behaviour of the glassy form may possibly be due to the presence of both crystal forms. The amorphous structure agrees with this view, since it is certainly not to be ascribed to a higher molecular weight, as other properties, *e.g.* density, lie between those of the octahedral and monoclinic forms. The melting point, as is to be expected in such a mixture, lies lower than that of either component. In the glassy form the particles of octahedral arsenic

[1] C. C. Miller, *J. Chem. Soc.*, 1928, 1847.

serve as nuclei for the conversion of monoclinic particles into octahedral, since in time arsenic glass becomes milky, and it breaks down on rubbing into powdery octahedral crystals. This occurs especially easily in the presence of moisture; in aqueous solution all forms are converted into octahedra.

Properties.—The density is sometimes higher in the octahedral form and sometimes in the monoclinic, *e.g.*:

For octahedral As_2O_3 3·64   monoclinic As_2O_3 4·0.

„ Sb_2O_3 5·2   „ Sb_2O_3 3·7.

The solubility of octahedral As_2O_3 is noticeably less than that of the monoclinic. The solubilities of the four trioxides diminish very markedly with rising atomic weight as the higher ones, unlike arsenic, do not function as acid anhydrides. P_2O_3 dissolves to a considerable extent in cold water to form $P(OH)_3$, but only very slowly; if hot water is used it dissolves with almost explosive violence, undergoing decomposition, similar to that which occurs on dry heating (see below). As_2O_3 dissolves with much more difficulty, *e.g.* in 100 g. water:

At temperature   2°   25°   40°   100°

As_2O_3 .   .   1·2   2·0   3·0   6 g.

At 15° only 0·001 g. Sb_2O_3 dissolves and Bi_2O_3 is practically insoluble.

Phosphorus trioxide also dissolves so easily in organic solvents (C_6H_6, CS_2, etc.) that it is possible to determine its molecular weight in these solutions; the formula P_4O_6 is confirmed. As_2O_3 dissolves in alcohol even less readily than in water, and nitrobenzene dissolves only one-fiftieth of its weight. The other oxides do not dissolve in organic media. The solution of arsenic in water is slow because water wets it only with great difficulty. Powdered arsenic trioxide floats on water in spite of its high specific gravity, owing to the air which adheres to it; if, however, the surface tension is altered by the addition of H˙ or OH′ ions it becomes wetted and solution takes place, chemical change no doubt also being involved.

The colour of the trioxides deepens with increase in the atomic weight of the non-metal. Those of the lighter elements are white, that of Bi_2O_3 pale lemon yellow. On heating, however, as is so often found, the colour deepens even in Sb_2O_3, which becomes yellow and melts to a yellowish liquid, while Bi_2O_3 goes from orange to reddish brown.

The melting points rise in the same order. That of the lightest member (P_2O_3) is 23·8°, and of the heaviest (Bi_2O_3) 820°; that of As_2O_3 cannot be established under normal pressure, since the homogeneous modifications sublime on heating; a mixture of them (glassy arsenic) is fusible. The vapour of pure arsenic trioxide is odourless, while P_2O_3 has the odour of garlic even in the solid state, but this smell may be

that of its decomposition products. The boiling point of the liquid trioxide is known only for P_2O_3 ($173 \cdot 10°$). In the gaseous condition they all have the molecular formula X_4O_6, but the double molecules break up at very high temperatures. Sb_4O_6 exists in the undissociated form up to $1560°$; the behaviour of As_4O_6 has been studied in detail.[1] The vapour density referred to air is as follows:

Temp.	.	.	518°	851°	1059°	1450°	1732°
d.	.	.	13·7	13·2	12·8	9·4	7·3

At the highest of these temperatures it has almost diminished to the value corresponding to the formula As_2O_3.

Of these oxides, only As_2O_3 seems to be able to enter complex compounds as a neutral component; it then behaves like SO_3 (p. 548), but the compounds containing arsenic are often distinguished by remarkable insolubility and stability. Weinland and Gruhl[2] assume that the As_4O_8 is attached to the halogen radical; compounds of the following types are known :

$$\overset{\text{I}}{M}[X(As_2O_8)] \qquad M[X(As_2O_8)_2] \qquad \overset{\text{II}}{M}[X(As_2O_8)_2]_3$$
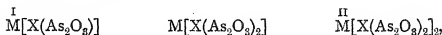
of which the third is distinguished by the high water content of its salts (12 mols.); X can be chlorine, bromine, iodine or thiocyanogen. The alkali compounds in particular are noteworthy because of their great stability and sparing solubility, and are always formed when arsenious acid and an alkali halide are allowed to react in acid or neutral solution, and also from an arsenite and a halogen salt.

The Tetroxides.—The chemical character of the tetroxides has been described on p. 705. Those of arsenic and bismuth are not definite compounds, but may be regarded as mixtures of the tri- and pent-oxides, particularly as their composition does not in general correspond to the tetroxide formula. The glassy appearance of the arsenic compounds and the non-crystalline form of the bismuth oxide mixtures is confirmatory evidence. Antimony tetroxide, Sb_2O_4, was thought to be a definite compound, but has recently[3] been shown to be, in part, $Sb^{III}O(OH), Sb^{V}_2O_5$. Antimony tri- and pent-oxides are both converted into Sb_2O_4 if they are roasted in air at a moderate temperature. At a suitable temperature (e.g. $750°$) the oxygen pressure of Sb_2O_4 is less than that in the atmosphere, while that of Sb_2O_5 is greater. Sb_2O_5 therefore gives up oxygen, but it does not decompose beyond the Sb_2O_4 stage. Sb_2O_8, the oxygen pressure of which is naturally less than that of Sb_2O_4, must take up oxygen at this temperature, especially as this reaction proceeds exothermally. Sb_2O_4 is stable over a wide temperature

[1] H. Biltz, Z. physikal. Chem., 1896, 19, 417.
[2] Arch. Pharm., 1917, 255, 467.
[3] Ann. Rep. Chem. Soc., 1938, 35, 119.

range, though it seems to be able to give mixtures with Sb_2O_3 and Sb_2O_5 near the limits of this temperature interval, and for this reason is not now used in the quantitative estimation of antimony.

Antimony tetroxide forms a powder, the properties of which are intermediate between those of Sb_2O_3 and Sb_2O_5; this applies also to its colour, which is pale yellow and becomes a little deeper on heating. It may be regarded as an antimonous salt of antimonic acid; quadrivalent antimony is probably not present in it, since the compounds of quadrivalent antimony, e.g. K_2SbCl_6, are very deeply coloured (pp. 748, 757).

Phosphorus tetroxide is the most definite substance in this group. On sublimation it forms brilliant crystals, which boil at 180° in a vacuum and correspond to the formula P_8O_{16} in the gaseous state, even at 1400°. When dissolved in water it gives phosphorous and phosphoric acids; it is very hygroscopic. Since the direct conversion $P_2O_5 \rightleftharpoons P_2O_3 + O_2$ cannot be carried out by calcining in air on account of the volatility of the oxides, P_2O_4 cannot be obtained by the method used for Sb_2O_4. It is therefore prepared by heating P_2O_3 in a closed tube, preferably at 290°. Then, and even at lower temperatures, P_2O_3 decomposes into free phosphorus and the higher oxide, as so often happens with substances of an intermediate degree of oxidation (cf. p. 376). If this splitting up of P_2O_3 is carried out in the presence of water (or alkali) reduction proceeds as far as PH_3, which is formed as well as phosphorous and phosphoric acids.

The Pentoxides.—Phosphorus pentoxide is formed when phosphorus is burnt in an adequate supply of air; P_2O_3 also ignites at 50° in oxygen and burns to form P_2O_5. The other pentoxides are formed by dehydrating the acids derived from them by the wet method. The combustion of phosphorus may readily be carried out by introducing a wick into molten phosphorus, and igniting it after it is saturated with the liquid. The product of combustion always contains more or less trioxide as a by-product, from which the pentoxide is freed by sublimation in oxygen. Pure phosphorus pentoxide is absolutely odourless. It occurs in two or more modifications, which give a glassy mixture when they are incompletely converted into one another; this is often treated as a special modification in the literature on the subject. When formed at lower temperatures, P_2O_5 forms voluminous snow-white flocks, without a recognisable crystalline structure, the vapour pressure being equivalent to one atmosphere at 250°, so that it sublimes. If it is superheated (to 440°) it gradually becomes a crystalline powder, which is much less volatile and melts at a red heat. The vapour pressure of this form depends on its previous history, as with certain forms of SO_3 (cf. p. 568). It vaporises only at a white heat and yields the crystalline form on cooling again. This seems to be able to dissolve the flocculent or perhaps a third form which is stable at still higher temperatures, since after digestion for some time at red heat the glassy

mixture is obtained. A. N. Campbell and A. J. R. Campbell[1] consider that the vitreous variety is the only homogeneous solid modification of phosphoric oxide. The glass of containing vessels catalyses the changes between the modifications. At 1400° the vapour corresponds to the formula P_4O_{10}; at lower temperatures the polymerisation seems to be somewhat greater.

The great ease with which it becomes hydrated with water is characteristic of P_2O_5. It is therefore employed as a powerful drying agent, and is also useful in the preparation of many acid anhydrides from their respective acids. Thus SO_3 may be distilled from a mixture of it with sulphuric acid, N_2O_5 obtained by its action on nitric acid, etc. For such purposes the flocculent form is the most effective, partly on account of its large surface. This form gives a clear solution in water accompanied by violent hissing due to the heat evolved on hydration, while the crystalline form does not immediately give a clear solution, but first forms transparent gelatinous little clots, which, however, soon pass into solution. Phosphorus pentoxide phosphoresces in the dark after it has been illuminated; this phosphorescence is very bright at low temperatures.

The other pentoxides, As_2O_5, and Sb_2O_5, are obtained by dehydrating their hydrates at dull red heat, when both form amorphous powders. Arsenic pentoxide is white and fusible; antimony pentoxide pale lemon yellow, infusible and insoluble in water. It dissolves with difficulty in acids after it has been ignited, and is particularly insoluble in nitric acid. Bismuth pentoxide has not yet been obtained pure, but contains both the lower oxide and alkali, the content of which may be attributed to its acidic nature or to its colloidal form. Its composition varies between the formulae Bi_2O_4 and Bi_2O_5.[2] It is a reddish brown or scarlet red (hydrated) substance obtained by the oxidation of an aqueous alkaline suspension of Bi_2O_3 with many oxidising agents: $K_3Fe(CN)_6$, H_2O_2, $KMnO_4$, persulphates, hypochlorites, etc.; it may also be formed in the dry way by fusion of the trioxide with caustic potash and chlorate in the air.

The Acids of Phosphorus, Arsenic, Antimony and Bismuth

Of the following acids only those of phosphorus and of quinquevalent arsenic are known in the free state. The others tend to decompose to form anhydrides. Some hydrates of the acids described in the literature owe their water content to the colloidal condition of the oxides. The anions, which are stable in alkaline solution, are

[1] *Trans. Faraday Soc.*, 1935, **31**, 1567.
[2] Gutbier and Bünz, *Z. anorg. Chem.*, 1906, **48-50**; Hauser and Vanino, *Z. anorg. Chem.*, 1904, **39**, 381.

derived (for As, Sb and Bi hypothetically) from the following acids:

H_3PO_2 hypophosphorous acid;

H_3PO_3 phosphorous, H_3AsO_3 arsenious, H_3SbO_3 antimonious acids;

H_4PO_3 hypophosphoric acid;

H_3PO_4 phosphoric, H_3AsO_4 arsenic, H_3SbO_4 antimonic, $HBiO_3$ bismuthic acid;

$H_4P_2O_8$ perdiphosphoric acid;

H_3PO_5 permonophosphoric acid.

Besides compounds which contain ions derived from these acids, a very large number of compounds are known which may be considered as partially dehydrated forms, and of which the more notable members are the pyro- and meta-acids, especially of phosphorus (*cf.* p. 725 *et seq.*).

In considering the constitution of the acids of phosphorus, H_3PO_4, H_3PO_3 and H_3PO_2 may be taken to form the first three members of the continuous series:

$$\left[PO_4\right]H_3 \qquad \left[P{O_3 \atop H}\right]H_2 \qquad \left[P{O_2 \atop H_2}\right]H \qquad \left[P{O \atop H_3}\right] \qquad \left[PH_4\right]X$$

Phosphoric   Phosphorous   Hypophosphorous   Phosphine   Phosphonium
acid.   acid.   acid.   oxide.   salt.
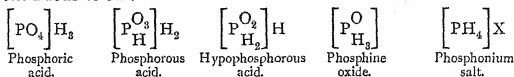
The co-ordination number of phosphorus is 4. If all four co-ordination positions are filled by oxygen, the complex has three negative charges—phosphoric acid is tribasic. If the oxygen content is diminished by one atom, a hydrogen atom enters the nucleus and gives phosphorous acid, which is dibasic. If a further nuclear oxygen atom is displaced by hydrogen, the univalent ion of hypophosphorous acid is formed, and finally by the entrance of a third hydrogen atom into the nucleus, the neutral molecule PH_3O is produced, a form which has hitherto been obtained only in organic derivatives. If the last oxygen atom is also replaced by hydrogen, the nucleus becomes the univalent positive radical of the monobasic phosphonium salts, in which the complex radical is combined with an acid residue.

Perdiphosphoric acid and permonophosphoric acid are phosphoric acids in which an O atom is replaced by an -O-O- group. The former corresponds to perdisulphuric acid and the latter to Caro's acid.

$$H_2\left[O_3P.O—O.PO_3\right]H_2 \qquad\qquad \left[P{O.O \atop O_3}\right]H_3$$

Perdiphosphoric acid.   Permonophosphoric acid.
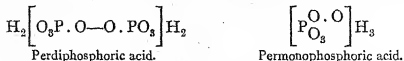
If it is desired to express these relationships by electrovalency formulae, it may be done as follows:

H_3PO_2. H_3PO_3. H_3PO_4.

$H_4P_2O_8$. H_3PO_5.
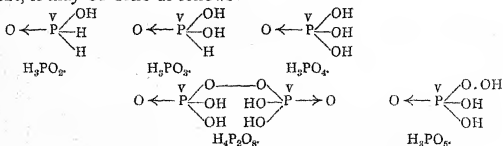
The observed basicity of the acids is in complete agreement with the formulae given. Phosphorous acid is formed by hydrating the trioxide or by hydrolysing the trichloride:

$$P_2O_3 + 3H_2O \longrightarrow 2H_3PO_3, \qquad PCl_3 + 3H_2O \longrightarrow P(OH)_3 + 3HCl,$$
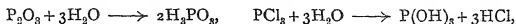
but these modes of formation do not indicate why the phosphorus is not tervalent in the acid, according to the constitution:

$$P\begin{cases}OH\\OH\\OH\end{cases}$$

There are also esters of phosphorous acid in which all three hydrogen atoms are replaced by aliphatic radicals, e.g. $P(O.CH_3)_3$, $P(O.C_2H_5)_3$, which is thus in agreement with the assumption that the phosphorus is tervalent. The phenomenon can be explained by changes of the isomeric forms or by an equilibrium existing between the ordinary and a reactive form.[1] There is evidence also for tautomeric forms of hypophosphorous acid.

Hypophosphoric acid, H_2PO_3, does not really come in this series. It is a dibasic acid, the formula of which will be more closely considered later (p. 716).

Only phosphorous and phosphoric acids can be regarded as hydrates of known anhydrides; the anhydrides of the other acids are not known, and the acids undergo extensive decomposition during dehydration.

The acids of arsenic, antimony and bismuth, as well as their salts, correspond to those of phosphorus in their structure. The reason why the series is less complete is not clear, though it is usual for the variety of acids to decrease rapidly below the third series in the periodic system. On the other hand, more acids of sulphur and selenium are known than of chlorine or bromine.

Hypophosphorous Acid, H_3PO_2.—Hypophosphorous acid is a product of hydrolysis of phosphorus. Just as chlorine is hydrolysed by water to form HCl and HClO, and sulphur to give H_2S and H_2SO_2, so phosphorus on hydrolysis yields hydrogen phosphides and hypophosphorous acid. The equilibrium of this hydrolysis, as with chlorine and sulphur, does not favour the formation of the acid in neutral solution. Hence, in the preparation of hypophosphites, yellow phosphorus is boiled with a solution of the hydroxides of the alkalis or alkaline earths, when the gaseous phosphine which is formed escapes, the solid one is deposited and the hypophosphite remains in solution. The reduction $P + H_3PO_4 \longrightarrow H_3PO_2$ also takes place between phosphorus and phosphoric acid, and at 200° affords a method for the preparation of hypophosphorous acid. No

[1] See Mitchell, J. Chem. Soc., 1920, 957, 1322; 1921, 1266; 1922, 1624; 1923, 629, 2241; 1924, 564, 1013; 1925, 336.

other methods of reducing phosphoric to hypophosphorous acid have been described.

The free acid is obtained from one of its salts by adding an acid which gives an insoluble salt with the metal, e.g. from the barium salt with sulphuric acid or from the lead salt with sulphuretted hydrogen. The acid crystallises on evaporation in large white leafy crystals of m.pt. 26·5°, which are hygroscopic and very easily soluble in water. Like most compounds of intermediate state of oxidation, it decomposes on heating into the end members of the series: $4H_3PO_2 \longrightarrow 2PH_3 + 2H_3PO_4$, though the decomposition does not proceed direct according to the above reaction, but yields P_2H_4, elementary phosphorus, H_3PO_3, etc. The salts show an analogous behaviour on heating.

Hypophosphorous acid is a strong reducing agent; its position in the oxidation and reduction series is close to that of hydrogen. Silver, gold, the platinum metals and even mercury, copper and bismuth are deposited by it in the elementary condition. It also has the property of passing into phosphorous acid with the liberation of hydrogen without artificial heating, mostly in alkaline solution; this reaction, however, takes place in neutral solution when certain catalysts are present, and thus the palladium precipitated by hypophosphorous acid can further catalyse unlimited quantities of the acid into H_2 and H_3PO_3, even if it is already aged[1]; finely divided copper has a similar but weaker effect. It was previously thought that metallic hydrides, formed as intermediates, stimulated the spontaneous decomposition of hypophosphorous acid. In the red deposit of copper which hypophosphites give in solutions of copper salts, a hydride of copper, CuH_2, seemed to be present; it has a noticeable hydrogen content when precipitated from acid, but not from alkaline solutions. The existence of the copper hydride as a chemical compound has been questioned[2] (cf. p. 875). Hypophosphorous acid is convertible into phosphoric acid by all kinds of oxidising agents; but it has so far been reduced to PH_3 only by means of nascent hydrogen.

All the salts of hypophosphorous acid are monobasic. They are all, in contrast to the phosphates, easily soluble in water, those of the alkaline earths being least soluble. The alkali and alkaline earth salts are anhydrous or contain little water, while those of other bivalent metals usually contain 6 mols. of water of crystallisation and also form hexammines with ammonia. The salts are thus comparable with those of the stronger monobasic acids in their solubilities and ability to form addition compounds, and are quite different from those of phosphoric acid. They also show reducing properties in solution, and with strong oxidising agents such as $KClO_3$ or KNO_3 the mixtures

[1] Engel, Compt. rend., 1890, 110, 786.
[2] Sieverts and Lössner, Z. anorg. Chem., 1912, 76, 1.

can act as powerful explosives. The poisonous properties of phosphorus, which also appear to a lesser degree in PH_3, have almost completely disappeared in the hypophosphites.

Phosphorous Acid, H_3PO_3.—This acid, the true hydrate of phosphorus trioxide, and obtainable from it by the action of water, is always formed if less highly oxidised compounds of phosphorus or the element itself are exposed to moderate oxidation. Thus PH_3 reacts with dry oxygen under reduced pressure with brilliant luminosity thus: $2PH_3 + 3O_2 \longrightarrow 2H_3PO_3$. Elementary phosphorus, if kept in contact with copper sulphate solution, reduces it to copper (subsequently forming a phosphide) and is converted to phosphorous acid; it reacts similarly with dilute nitric acid, but phosphoric acid is always formed in addition by further oxidation. Phosphorous acid is also formed by the oxidation of hypophosphorous acid with atmospheric oxygen, or with the salts of the more noble metals. These methods have little practical significance as the acid can readily be prepared by the hydrolysis of phosphorus trichloride, PCl_3, which is to be regarded as the acid chloride of phosphorous acid: $PCl_3 + 3H_2O \longrightarrow P(OH)_3 + 3HCl$. This reaction, unlike most of the other methods of preparation, gives no other acids of phosphorus as by-products.

The free acid may be obtained as colourless deliquescent crystals by evaporating the solution. It can readily be oxidised to phosphoric acid and therefore acts as a reducing agent. Its reducing power is not much less than that of hypophosphorous acid; like this acid, it reduces the salts of the noble metals, and even copper salts, to the metal. It is characteristic of phosphorous acid that the reduction of mercuric chloride by an excess of it yields a white precipitate of mercurous chloride. Like hypophosphorous acid, it undergoes auto-reduction and oxidation on heating, leading on the one side to phosphoric acid and on the other to various reduction products, even to PH_3. No hypophosphorous acid is formed, since this acid is already decomposed at the temperature at which phosphorous acid breaks up. An analogous decomposition is shown by phosphites. It is, however, possible to isolate an intermediate stage when the decomposition is limited to the elimination of one molecule of water, giving a pyrophosphite: $2M_2HPO_3 \longrightarrow M_4P_2O_5 + H_2O$. A meta-phosphorous acid, HPO_2, with still less water has also been described.

Phosphites of the alkalis are soluble in water, all the others being very sparingly soluble; they are not amorphous like the phosphates, but crystalline like the hypophosphites, mostly with a definite water content. Phosphites of tervalent metals are also known, from which it may be concluded that phosphorous acid is not a weak acid. In fact, conductivity determinations show it to be of medium strength, not very different from that of hypophosphorous acid. It can form complexes with other acids, e.g. with acids containing metals, which

appear as "polyacids." Thus the "acid" phosphites must be regarded as salts of a polyacid, $H_6[H(PO_3H)_2]$, which are formed from the normal salts when excess of phosphorous acid is present, and in contrast to them are easily soluble.

Hypophosphoric Acid, $H_4P_2O_6$; this acid is also written as H_2PO_3, but the evidence supports the double formula (see below). Hypophosphoric acid is formed, together with phosphorous and phosphoric acids, by the oxidation of phosphorus with dilute nitric acid, especially in the presence of salts of the nobler metals ($AgNO_3$, $Cu(NO_3)_2$). Although contaminated with these two acids, and obtained in smaller yield, it can easily be separated from them by its acid sodium salt, $Na_2H_2P_2O_6 . 6H_2O$, which is difficultly soluble. Oxidation by atmospheric oxygen gives good yields of hypophosphoric acid if care is taken that the exothermal process of oxidation is completed as slowly as possible, so that the temperature remains low. This is effected by keeping sticks of phosphorus, half covered with water, in a loosely closed vessel. Possibly phosphorous acid is formed first, and is then partially converted by the air into hypophosphoric acid. It can be prepared more rapidly by dropping bleaching powder solution on to red phosphorus. It is also obtained electrolytically by electrolysing faintly acid solutions with anodes of copper phosphide.[1]

The free acid, which is obtained by decomposing its barium salt with sulphuric acid, forms easily soluble white crystals, which melt at $70°$, and exists as various hydrates as well as in the anhydrous condition. The acid anhydride is not known; phosphorus tetroxide, P_2O_4, cannot be considered as such, since it neither yields hypophosphoric acid if treated with water, nor is the acid converted into P_2O_4 by dehydration. The acid decomposes very easily and spontaneously in aqueous solution, into phosphorous and phosphoric acids: $H_4P_2O_6 + H_2O \longrightarrow H_3PO_3 + H_3PO_4$, and was regarded as derived from one molecule of phosphoric and phosphorous acids by the elimination of one molecule of water, being thus the pyro-acid, $(HO)_2OP . O . P(OH)_2$. The unimolecular form,[2] $OP(OH)_2$, however, was supported by the change in conductivity of its salts on dilution, which resembles that of the salts of dibasic acids much more than that of the tetrabasic ones. On the other hand, the conductivity of pyrophosphoric acid (supposed to be tetrabasic) shows a similar behaviour to that of hypophosphoric acid[3] and the salts of these two acids also have many similar features. The neutralisation curve also suggests that hypophosphoric acid is tetrabasic. The monomolecular formula is suggested by the heat of fusion and the specific cohesion at the melting point,[4] but esters[5] of the formula

[1] Salzer, *Ann.*, 1877-1886.   [2] Rosenheim and Pinsker, *Ber.*, 1910, 43, 2003.
[3] W. D. Treadwell and G. Schwartzenbach, *Helv. Chim. Acta*, 1928, 11, 405.
[4] Walden, *Z. Elektrochem.*, 1908, 14, 718.
[5] Rosenheim and Pritze, *Ber.*, 1908, 41, 2708.

$PO_3(CH_3)_2$, prepared by the interaction of alkyl halides and silver hypophosphate could not be confirmed.[1] Arbusow and Arbusow, however, prepared the pure ester, $Et_4P_2O_6$, by the interaction of sodium diethyl phosphite $(EtO)_2P.ONa$ and bromine, and Bell and Sugden examined the magnetism of salts of the acid. They are all diamagnetic, supporting an even electron formula, whereas the acid H_2PO_3 (25 valency electrons) and its salts, containing an odd number of valency electrons, should be strongly paramagnetic.

In addition to $Na_4P_2O_6$, the salts $Na_3HP_2O_6$, $Na_2H_2P_2O_6$ and $NaH_3P_2O_6$ are known. $K_3H_5(PO_3)_4$ and $Na_5H_3(PO_3)_4$ have also been found, for which the fourfold formula could be claimed with equal right. But hydrochloric acid and nitric acid are not given the formulae H_2Cl_2 and $H_2(NO_3)_2$ because acid salts of these acids exist.

On account of this tendency to polymerise, the structure of the hypophosphates is especially varied; all possible "acid" salts can exist, of which examples have already been given in the above types; the formation of "double" hypophosphates, which contain several metals and perhaps hydrogen atoms as well, is particularly easy. The following compounds may serve as an example:

$$NiNa_2(PO_3)_2, \qquad K_2H_4Cu(PO_3)_4, \qquad K_6H_5Ni(PO_3)_8.$$
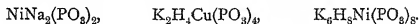
The alkali salts and an acid barium salt are soluble in water; all other hypophosphates are difficultly soluble; some are not easily soluble in acetic acid. The insolubility of the barium salts in acetic acid distinguishes them from phosphates. The thorium salt ThP_2O_6 is very characteristic and is practically insoluble in strong mineral acids. The salts are very closely related to the phosphates, from which they are distinguished by their crystalline structure. The silver and lead salts are white. The normal alkali salts are hydrolysed in water, and the ammonium salt gives off ammonia even in the solid condition.

Their chemical behaviour characterises the hypophosphates as intermediate between the phosphites and phosphates. They reduce only the strongest oxidising agents ($KMnO_4$), but not the salts of the noble metals; on dry heating they give the phosphate and reduction products, but can withstand higher temperatures than the phosphites.

All the phosphorus acids described so far are products of partial oxidation. They may be decomposed by heat into higher and lower members of the oxidation series; they have reducing powers which diminish step by step, with increasing oxygen content, and which no longer exist in phosphoric acid. The solubility of their salts decreases with increase in the oxygen content, and then increases again, so that the hypophosphites are very easily soluble, some of the phosphites

[1] Arbusow and Arbusow, *J. prakt. Chem.*, 1931, **130**, 121; Bell and Sugden, *J. Chem. Soc.*, 1933, 48.

are insoluble, the hypophosphates are even sparingly soluble in acetic acid, while the hypophates are again more easily soluble in acids. Hypophosphites and phosphites are always crystalline, the insoluble hypophosphates are nearly always precipitated in the amorphous state, but crystallise later, while phosphates preserve their amorphous form for a much longer time. Hypophosphoric, like phosphoric acid, tends to form polymerised salts. The tendency to form poly-acids with other acids, although present in all the acids of phosphorus, is most marked in phosphoric acid, and leads to characteristic reactions. Finally, the strength of the acids, according to Abegg and Bodländer, decreases from hypophosphorous to phosphoric acid, in accordance with their polymerisation; this is somewhat remarkable, as in other series the greatest acidity is attained with the highest oxygen content. This is seen from the following table, in which the conductivities (Λ), expressed in reciprocal ohms, are given for a gram molecule of the various acids in $N/32$ solution. The value for the somewhat weaker arsenic acid is added for comparison:

	H_3PO_2 (18°)	H_3PO_3 (25°)	H_3PO_4 (25°)	H_3AsO_4 (25°)
Λ	281	257	156	125.5

The tendency of the phosphorus acids to lose water and to form definite partial anhydrides is in good agreement with their low strength; it makes their chemistry particularly involved.

Hydrates of Phosphorus Pentoxide

H_3PO_4	i.e.	$P_2O_5, 3H_2O$	Orthophosphoric acid.
$H_4P_2O_7$	,,	$P_2O_5, 2H_2O = 2H_3PO_4 - 1H_2O$	Pyrophosphoric acid.
$H_5P_3O_{10}$	,,	$3P_2O_5, 5H_2O = 3H_3PO_4 - 2H_2O$	Triphosphoric acid.
$H_6P_4O_{13}$	,,	$4P_2O_5, 6H_2O = 4H_3PO_4 - 3H_2O$	Tetraphosphoric acid.
HPO_3	,,	$P_2O_5, H_2O = nH_3PO_4 - nH_2O$	Metaphosphoric acid.

Some of these hydrates of phosphorus pentoxide are known in the free condition and some as their salts. It is possible that other intermediate hydrates exist.

The highest hydrate is orthophosphoric acid. The others may be considered as formed from it by the elimination of water: either one molecule of the ortho-acid loses one molecule of water to yield the meta-acid:

$$OP\left\langle\begin{array}{l}O\vdots H\\\vdots\\O H\\\\O H\end{array}\right. \xrightarrow{-H_2O} \quad O \leftarrow P\left\langle\begin{array}{l}O\\\\O H\end{array}\right.,$$
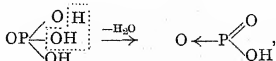
or condensation (i.e. molecular union by dehydration) occurs between two molecules of orthophosphoric acid by the elimination of one molecule of water, when the pyro-acid is obtained; or chain forma-

tion between more than two orthophosphoric acid residues takes place, in which one molecule of water is always split off between two molecules, when triphosphoric acid, tetraphosphoric acid and still higher condensation products are produced:
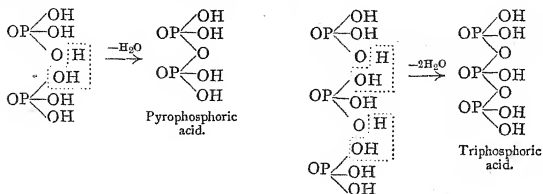
The most important of these dehydration products are the pyro- and meta-acids, which are most easily formed; the others have not been investigated in detail. The chemistry of the meta-acid is particularly varied, as it has a very strong tendency to form polymers $(HPO_3)_x$, so that there is a whole series of polymetaphosphoric acids with increasing molecular weight.

Orthophosphoric Acid, H_3PO_4.—This acid is formed as a by-product in all the oxidation methods used in the preparation of phosphorous or hypophosphoric acids; it becomes the main product if the energy of the oxidation increases. Since these lower acids have a considerable reduction potential, a very large number of oxidising agents convert them and also free phosphorus or even phosphine into phosphoric acid. For practical purposes only nitric acid and atmospheric oxygen are used, and yellow phosphorus as the substance to be oxidised. This has an almost explosive reaction with strong nitric acid, and hence the acid used for the preparation of phosphoric acid must not exceed a density of 1·2. Phosphorous acid is first formed, and the phosphoric acid is always mixed with it after the operation is ended, and is only completely oxidised after evaporation and renewed treatment with nitric acid.

Phosphoric acid can also be obtained by the hydrolysis of yellow phosphorus. When phosphorus is heated in water vapour above 200° (the reaction has been investigated up to 1000°) phosphoric acid and hypophosphorous acid are first formed but the latter splits up into phosphoric acid and phosphine, which in its turn is decomposed into phosphorus and hydrogen. Hence the final products of this hydrolysis are hydrogen and phosphoric acid.

The natural or commercial phosphates are used rather than free phosphorus for the preparation of crude phosphoric acid. Calcium phosphate (rock phosphate, bone ash, basic slag) is most commonly employed.

If soluble salts of phosphoric acid are required—the sodium compound is used most, excepting "superphosphate" (p. 722)—it is sufficient to ignite the calcium compound with Na_2SO_4; insoluble calcium sulphate and soluble sodium phosphate are formed, and the latter is extracted with water. In order to obtain the free acid the calcium phosphate is decomposed by heating with concentrated sulphuric acid. Here again calcium sulphate separates as an insoluble product, and the excess sulphuric acid can be removed from the remaining liquid by evaporation.

The phosphoric acid forms a syrup which crystallises on cooling. The clear colourless crystals which melt at about 41° often appear only after inoculation, since the syrup has a great tendency to be supercooled. It is very difficult to crystallise it if a little water is present, as this lowers its melting point considerably; but when the water content is increased to 0·5 mol. H_2O per mol. H_3PO_4, it easily solidifies, since the composition corresponds to a definite hydrate.

Phosphoric acid is a very weak acid. In conductivity determinations the dissociation of only one hydrogen atom is observed; the degree of ionisation, in comparison with that of the other phosphorus acids, 's evident from the table on p. 718. The primary salts of phosphoric acid, MH_2PO_4, are always acid in reaction, but the secondary alkali salts show strong hydrolysis and an alkaline reaction, which is naturally even greater in the tertiary (normal) salts. The formation of the normal salts indicates that the third hydrogen atom can dissociate. If aqueous phosphoric acid is neutralised in the presence of litmus and then allowed to crystallise, a salt intermediate between the primary and secondary salts is obtained, $M_3H_3(PO_4)_2$, a well-defined sesquiphosphate, which may be recrystallised from solution undecomposed, and is again soluble to give a neutral reaction. Further, on crystallising primary salts with the free acid, compounds which are even more acidic than the primary salt are obtained. The series

$M_6(PO_4)_2$	*i.e.*	$2M_3PO_4$	alkaline
$M_4H_2(PO_4)_2$	,,	$2M_2HPO_4$	,,
$M_3H_3(PO_4)_2$	,,	M_3PO_4, H_3PO_4	neutral
$M_2H_4(PO_4)_2$	,,	$2MH_2PO_4$	acid
$MH_5(PO_4)_2$	,,	MH_2PO_4, H_3PO_4	,,
$H_6(PO_4)_2$	,,	$2H_3PO_4$	,,

is thus obtained. The salt formation of phosphoric acid thus follows the lines described for hypophosphoric acid (p. 717).

Unimolecular esters of phosphoric acid are well known. The marked tendency of phosphoric acids to form heteropoly-acids with other acids (phosphomolybdic acid, phosphotungstic acid, etc.; *cf.* p. 500) makes it probable that isopolyacids may also be derived from it.

The sparing solubility of its salts is also in good agreement with polymerisation.

Phosphoric acid also resembles the lower acids of phosphorus in many other physical properties; e.g. its heat of dissociation is positive, like that of hypophosphorous acid. Again, its heat of neutralisation is high, and its conductivity first increases with rise in temperature, and then falls again, with a maximum at about $74.5°$.

Phosphoric acid is miscible with water in all proportions. The mixtures have the following densities:

H_3PO_4 .	10	25	50	75	90	100 per cent.
d.	1.06	1.15	1.34	1.60	1.78	1.88

Phosphates.—Only the phosphates of the alkalis and the primary salts of the alkaline earths are soluble in water. It must, however, be remarked that the tertiary phosphates of the heavy metals are almost without exception stable to water, and this leads to the conclusion that their acid salts are also more soluble than the tertiary ones. Thus silver nitrate, for example, gives only the tertiary salt with secondary phosphates; the acid phosphate is only obtainable with a large excess of free phosphoric acid. The same effect is observed for almost all the other heavy metals. In the phosphates of the alkaline earths and some other metals, however, the difference in solubility is less, so that it is possible to obtain the acid salts at least for a short time. If a solution of calcium chloride is decomposed with NaH_2PO_4, it remains completely clear at first, and becomes turbid only on warming or on standing, owing to the deposition of the secondary or tertiary salt. A solution of a calcium or barium salt with a secondary alkali phosphate likewise gives a precipitate which consists of a secondary alkaline earth phosphate, which is gradually (but especially quickly on heating) converted into the tertiary salt, since this is the most sparingly soluble. Free acid must be formed in solution, so that, if the neutral calcium salt solution and the alkaline sodium phosphate solution are mixed hot, the liquid acquires an acid reaction:

$$3Na_2HPO_4 + 3CaCl_2 \longrightarrow Ca_3(PO_4)_2 + 6NaCl + H_3PO_4.$$
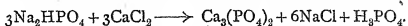
If the solution contains an excess of H˙ ions, the formation of PO_4''' ions is repressed, and indeed concentrations of all the acidic ions are repressed. H_2PO_4' may, however, be present in sufficient quantity for the solubility product to be exceeded. In this case the tertiary salt does not separate, for it is soluble in weak acids like acetic acid, and even in carbonic acid. The production of a sufficient quantity of PO_4''' ions is affected by all the concentration ratios. $Ca_3(PO_4)_2$ will be formed from a very concentrated solution of $Ca(H_2PO_4)_2$ but not from a dilute one, and with a certain excess of phosphoric acid it is possible to obtain $CaHPO_4$ as a solid phase, without subsequent conversion into the primary or tertiary salt. This happens, e.g. at $24°$, if the solution contains 1.44 millimols CaO and 2.36 millimols H_3PO_4. Even the addition of ammonium salts is sufficient

to reduce the concentration of OH' ions to such an extent that the tertiary salts dissolve.

If an acid solution containing phosphate and alkaline earth ions is treated with OH ions, the tertiary salt is immediately precipitated. For this reason the presence of phosphoric acid in the usual course of qualitative analysis interferes with the identification of the metals of the alkaline earths. On the addition of ammonium sulphide or ammonia the solution becomes alkaline, and the alkaline earth ions combine with the PO_4''' ions formed and separate as phosphates, together with the ordinary group precipitate. The phosphoric acid is therefore removed before adding ammonium sulphide.

The stable primary calcium phosphate, mixed with gypsum, is extensively used as "super-phosphate"; it is produced from powdered phosphorite and sulphuric acid. The soluble superphosphate has the advantage over the insoluble basic slag that the phosphoric acid becomes distributed through the soil in a much shorter time.

Some well-defined basic phosphates are known, the most important being basic slag, a crystalline calcium salt, $4CaO, P_2O_5$.

According to Werner,[1] certain compounds in which the phosphate has entered into the molecules of other salts as a neutral group are related to these basic salts. The best known of these are common minerals, such as apatite, $3Ca_3(PO_4)_2, CaF_2$. This prototype of an important group of compounds has the constitution:

$$[Ca\{Ca_3(PO_4)_2\}_3]F_2.$$
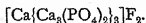
The negative fluoride radical can be replaced by others, such as chloride, bromide or iodide. Many other bivalent metals occur in minerals of the apatite type instead of calcium, e.g. Sr, Ba, Mn, Pb, Cd, Mg, and the phosphorus may be replaced by arsenic or vanadium, so that a very large group of compounds is possible, of which many members occur naturally as minerals, e.g. :

$$[Pb\{Pb_3(AsO_4)_2\}_3]F_2 \qquad\qquad [Pb\{Pb_3(VO_4)_2\}_3]Cl_2.$$
Mimetisite.   Vanadinite.
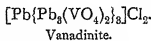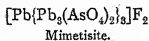
The closely related wagnerites are just as abundant; they differ from apatite in that not all six co-ordination positions are occupied by phosphate molecules. Wagnerite itself is a magnesium compound of the formula $[Mg\{Mg_3(PO_4)_2\}]F_2$; the magnesium in this compound may also be replaced by other bivalent metals—phosphorus by arsenic or vanadium, and fluorine by other halogens. The basic phosphate mentioned above, $[Ca\{Ca_3(PO_4)_2\}]O$, is connected with this group.

The phosphate radical itself may also occur in the negative radical forming the complex, making it more strongly negative. Such compounds probably occur in the complex ferric phosphates, which, according to Weinland and Ensgraber,[2] are derived from the acids
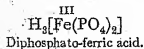
$$\overset{\text{III}}{H_3}[Fe(PO_4)_2] \qquad\text{and}\qquad \overset{\text{III}}{H_6}[Fe(PO_4)_3],$$
Diphosphato-ferric acid.   Triphosphato-ferric acid.
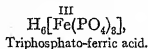
[1] Ber., 1907, 40, 4441.   [2] Z. anorg. Chem., 1913, 340, 84.

of which the ferric salt $\overset{\text{III}}{\text{Fe}}[\overset{\text{III}}{\text{Fe}}(PO_4)_2]$ is isomeric with ordinary ferric phosphate, though it differs in colour. The complex nature of the ferric phosphates is probable on other grounds, for when phosphoric acid is added to a solution of a ferric salt, coloured yellow owing to hydrolysis, the colour is immediately removed.

Of the normal phosphates, as remarked above, only those of the alkalis are appreciably soluble in water, but lithium shows its relationship to the alkaline earths, and its phosphate has such a small solubility that it may be used in the quantitative estimation of lithium. The solubility of the normal alkali phosphate increases with the atomic weight of the alkali, that of the phosphates of K, Rb and Cs being very considerable. On hydrolysis they are almost completely decomposed into the secondary phosphate and alkali hydroxide, and hence they hydrolyse esters almost as rapidly as the equivalent quantity of the free alkali hydroxide. On account of this weakness of the third hydrogen atom, the tertiary ammonium salt loses exactly 1 mol. of NH_3 on standing in air, and by using suitable indicators (phenolphthalein) phosphoric acid may be titrated with sodium hydroxide as a dibasic acid, as the colour change occurs just when the second hydrogen atom is neutralised.

Hydration and Solubility.—The water of crystallisation in the tertiary salts stable at room temperature is as follows:

Li	Na	K	Rb	NH_4	Cs	salt.
0·5	12	0	4	5	5	mols.

The tertiary salts do not crystallise very well, and consequently in commerce the secondary sodium salt and the primary potassium salt are preferred owing to the ease with which they crystallise; secondary potassium phosphate has not hitherto been generally obtained in the crystalline form, but, on the other hand, potassium phosphates even more acid than the primary (*cf.* p. 720) can be obtained quite well crystallised. The acid potassium, rubidium, caesium and ammonium salts all crystallise anhydrous, except the secondary rubidium and caesium phosphates, which can take up 1 mol. water. In spite of this they are all very easily soluble, the ammonium salts least of all; the secondary ammonium salt needs four parts of water for solution, and the primary even more at room temperature. The secondary sodium salt is distinguished by its high water content; up to 36·6° it contains 12 mols., and then passes into the heptahydrate; at 100° it still contains 1 mol. H_2O. Sodium salts are generally remarkable for their water of crystallisation, as in the sulphate, borate, phosphate, arsenate, carbonate, etc., which contain 10-12 mols. H_2O. The more acid sodium phosphates also contain water, viz. at room temperature:

NaH_2PO_4	$Na_3H_3(PO_4)_2$	$NaH_5(PO_4)_2$	
2	15	1	mol. H_2O.

Sodium ammonium hydrogen phosphate, microcosmic salt, $NaNH_4HPO_4$, which is important for the preparation of metaphosphates and in bead tests, contains 4 mols. water.

It is remarkable that a number of the very sparingly soluble metallic phosphates contain an appreciable quantity of water. In general, very sparingly soluble compounds, when not colloidal, are anhydrous. The water in these phosphates is not adsorbed, since some of them have well-defined crystalline forms and retain their water tenaciously even at high temperatures. Some of the most sparingly soluble tertiary salts are especially rich in water. The following formulae of various types of phosphates will serve as examples:

$Mg_3(PO_4)_2$, 8 and $22H_2O$	$Co_3(PO_4)_2$, $8H_2O$	$Fe_3(PO_4)_2$, $8H_2O$
$MgHPO_4$, $7H_2O$	$Ni_3(PO_4)_2$, $7H_2O$	$FeHPO_4$, H_2O
$Mg(H_2PO_4)_2$, $2H_2O$	$Cu_3(PO_4)_2$, $3H_2O$	$Fe(H_2PO_4)_2$, $2H_2O$
NH_4MgPO_4, $6H_2O$	$Pb_3(PO_4)_2$, $4H_2O$	$FePO_4$, $4H_2O$
	$Zn_3(PO_4)_2$, $4H_2O$	$Zn(H_2PO_4)_2$, H_2O
	$ZnHPO_4$, $2H_2O$	$AlPO_4$, $\sim 4 \cdot 5H_2O$.

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It is remarkable that a number of the very sparingly soluble metallic phosphates contain an appreciable quantity of water. In general, very sparingly soluble compounds, when not colloidal, are anhydrous. The water in these phosphates is not adsorbed, since some of them have well-defined crystalline forms and retain their water tenaciously even at high temperatures. Some of the most sparingly soluble tertiary salts are especially rich in water. The following formulae of various types of phosphates will serve as examples:

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NH_4MgPO_4, $6H_2O$	$Pb_3(PO_4)_2$, $4H_2O$	$FePO_4$, $4H_2O$
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converted into the metaphosphate $NaH_2PO_4 \longrightarrow H_2O + NaPO_3$. The well-known compound $Mg(NH_4)PO_4$ behaves similarly; it first loses ammonia: $Mg(NH_4)PO_4 \longrightarrow NH_3 + MgHPO_4$, and this on further heating forms the pyrophosphate, with loss of water: $2MgHPO_4 \longrightarrow H_2O + Mg_2P_2O_7$. It is possible to obtain pyro- and metaphosphates in pure condition by this method; but the elimination of water during the formation of metaphosphates from primary phosphates cannot be stopped sharply at the pyrophosphate stage. By heating free phosphoric acid alone to a definite temperature either pyro- or meta-phosphoric acid can be obtained :

$$2H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O, \qquad H_3PO_4 \longrightarrow HPO_3 + H_2O,$$

but before all the phosphoric acid is converted into pyrophosphoric acid a portion has already been further dehydrated to metaphosphoric acid. Even the latter cannot be obtained pure by further heating, as before all has been converted to metaphosphoric acid, some has lost more water and passed into phosphorus pentoxide. Thus in the dehydration of phosphoric acid, mixtures of the several stages of dehydration are always obtained. At low temperatures water is taken up again very slowly. In dilute solution at room temperature only 4 per cent. of pyrophosphoric acid is reconverted into orthophosphoric acid in two days, and after four months less than 50 per cent. Metaphosphoric acid does not behave very differently; it yields very little pyro-acid, but almost exclusively orthophosphoric acid on hydration. If pyrophosphoric acid is boiled with strong acids it is converted into the ortho-acid in a short time.

The pure acids can therefore be obtained only by the double decomposition of their salts, *e.g.* from the silver salts by hydrochloric acid or from the lead salts by sulphuretted hydrogen. If the solutions are carefully evaporated the acids do not become much hydrated. Metaphosphoric acid, however, has hitherto been obtained only as a glass, which is in agreement with its tendency to polymerise. It is probable that all the free solid metaphosphoric acids are mixtures of different highly polymerised products, so that their crystallising power is very small.

Pyrophosphoric acid is also crystallised with difficulty, and is usually obtained as a glass. Nevertheless, turbid sugar-like, crystalline forms have occasionally been observed, and it was then noted that the acid did not melt below 61°—a higher melting point than that of the ortho-acid. After melting it solidifies again in the crystalline state, but with difficulty.

The salts of this acid are better defined than the free acid. The pyrophosphates are obtained only in two stages of neutralisation— as quaternary and secondary salts, $M_4P_2O_7$ and $M_2H_2P_2O_7$. Of these, the alkali and thallium salts are soluble in water, the partially

deliquescent potassium salt being the most soluble. Bassett, Bedwell and Hutchinson [1] suggest that water molecules are distributed to form cations with even co-ordination numbers, and that, owing to molecular volumes being approximately equal $[M(H_2O)_4]^{..}$ may be replaced by $[Na_2(H_2O)_2]^{..}$ or $[M(H_2O)_2]^{..}$ by $2Na^.$. $Na_4P_2O_7 . 10H_2O$ is accordingly formulated as $[Na(H_2O)_4]_2^{..}[Na_2(H_2O)_2]^{..}[P_2O_7]^{''''}$. The quaternary alkali salts are slightly hydrolysed. Quaternary salts of other metals, most of which are described as powdery, are all insoluble in water, but the secondary salts are soluble and crystalline. The insoluble pyrophosphates dissolve in an excess of alkali pyrophosphate with the formation of complex compounds, which are comparable to the complex thiosulphates (p. 558). The formulae

$$Na_2CuP_2O_7, aq., \qquad Na_4Mn_2(P_2O_7)_2, aq., \qquad K_8Mn_2(P_2O_7)_3, aq.$$

may be quoted as examples.

The tri- and tetra-phosphoric acids (p. 718), $H_5P_3O_{10}$ and $H_6P_4O_{13}$, are not known in the free state, but their sodium salts are obtained by fusing together suitable quantities of sodium pyro- and meta-phosphates. They are probably not to be regarded as double salts of pyro- and meta-phosphates, but rather as special stages in dehydration, since they cannot be obtained by evaporating mixed aqueous solutions of pyro- and meta-phosphates. They decompose in solution, particularly on heating and in presence of acids or alkalis, giving pyro- and meta-salts. In general, their properties lie between those of the pyro- and meta-phosphates, but the tetraphosphate is distinct from the metaphosphate in the solubility of its silver salt in an excess of the sodium salt. The triphosphates also show solubilities which are different from those of the components ; e.g. chromium sulphate in a solution of triphosphate gives a precipitate much more easily than in one which contains a mixture of pyro- and meta-phosphates in the proportions required by the triphosphate formula. The double compounds of the formula $MNa_3P_3O_{10}$ (usually $+12H_2O$) are characteristic of the triphosphates; M is a bivalent metal such as Cu, Fe, Zn, Mn, Ni and Co, and these salts crystallise from fairly concentrated solutions of the sodium salt on the addition of heavy metal salts.

Metaphosphoric acid, HPO_3, and its salts possess the most complicated properties of all the acids of phosphorus, because, on the one hand, they have a strong tendency to polymerise, when varied products of high molecular weight can be formed, while, on the other hand, these products show isomerism through different arrangement within the individual molecules, so that varying constitutions may appear with the same molecular complexity. The relations of the metaphosphates are still so confused, in spite of numerous investigations,[2] that the practice of giving definite formulae for the products must be given up for the present.

The metaphosphates are formed by heating together the calculated quantities of phosphoric acid and metallic oxides. The properties of

[1] J. Chem. Soc., 1936, 1412.

[2] For example, Pascal, Comp. rend., 1923, 176, 1398 ; 1924, 178, 1541, 1906. Boullé, ibid, 1935, 200, 658, 832. Germain, Chim. et Ind., 1936, 35, 22.

the metaphosphate formed differ according to the nature of the oxide employed; they also vary with the temperature used. Metaphosphates are also formed on heating the primary ortho- or the acid pyrophosphates, with elimination of water (Graham):

$$MH_2PO_4 \longrightarrow MPO_3 + H_2O, \qquad M_2H_2P_2O_7 \longrightarrow 2MPO_3 + H_2O.$$

Here also the condition of the product formed is entirely dependent on the method of heating, and by changing the rate of cooling of the melt various highly polymerised products are produced. "Microcosmic salt," $NaNH_4HPO_4$, does not give a homogeneous metaphosphate on heating. If the ammonia and water are driven off a melt is obtained, which breaks down into two different salts when water is poured on to it. One is easily soluble in water and the other completely insoluble (Maddrell's salt). If heated further, it passes into a glassy form, which is likewise a mixture of several modifications. Fleitmann and Henneberg[1] attempted to estimate the molecular size from the formulae of the double salts obtained, but the salts of type $KNa(PO_3)_2$ were later shown to be tetrametaphosphates, $M_4(PO_3)_4$, since their conductivities, measured at the dilutions 32 and 1024 litres, differed by about 40 reciprocal ohms; for according to the Ostwald-Walden Rule the basicity of an acid is equal to the conductivity changes between these dilutions divided by 10. At 25° the conductivity is

Dilution	Na salt	K salt	NH₄ salt	Li salt
$N/32$.	85·6	102·8	100·2	81·7
$N/1024$.	126·2	146·7	142·9	123·3
Difference .	40·6	43·9	42·7	41·6

The double salts such as $NaCa(PO_3)_3$ and Maddrell's salt have been similarly regarded as trimetaphosphates with some degree of probability, but the constitution of still more highly polymerised metaphosphates has not yet been decided. It appears that polymerisation series with 2, 3, 4, 5, 6, 8, 10, 14 and other members have been identified. Several were first obtained in the form of heavy metal salts; the heavy metal may then be precipitated by sulphuretted hydrogen and the alkali salt formed from the product by addition of alkali hydroxide. Others again can only be prepared in the form of their alkali salts, from which the salts of the heavy metals may be obtained by precipitation. All are very clearly distinguished from one another by their appearance and the solubility of their members; some give well-crystallised salts, others do not crystallise under any circumstances. The crystalline and soluble salts are also clearly differentiated by specific reactions; thus the trimetaphosphates, $H_3(PO_3)_3$, give no precipitate with barium or silver salts, while the tetrametaphosphates give white precipitates with both.

[1] Ann., 1848, 65, 304.

It is remarkable that the alkali salts of some of the higher series are colloidal. Thus an alleged potassium sodium hexametaphosphate can be precipitated by alcohol as a rubbery substance; its 3 per cent. solution is thick like glycerine, and potassium or sodium chloride can precipitate it from solution like a colloid. Other salts belonging to other series are liquids like turpentine, which float on water and dry to horny masses in air. In some of them a part of the metal can only be exchanged with difficulty, so that they must be assumed to contain complexes such as $Na_2[Na_4(PO_3)_6]$. To this class belong Graham's original metaphosphate (soluble) and the interesting salt first prepared by H. Rose, $Ag_5NaP_6O_{18}$. It is remarkable that alkali metals are found inside the complex—a rare occurrence. This type of formulation is supported by the fact that the salt renders soluble calcium salts inactive, presumably owing to the formation of $Na_2[Ca_2(PO_3)_6]$; sodium hexa-metaphosphate, under the name of "Calgon," is accordingly used in water treatment for boilers, laundry work, etc. Naturally many kinds of isomers are conceivable for these complexes, so that the number of different metaphosphoric acids is due not only to the number of metaphosphoric acid molecules contained in them, but is also affected by their internal arrangement. The reaction which is generally used to differentiate between pyro- and meta-phosphates—the coagulating effect of metaphosphates on white of egg —points to their complex structure. Such a coagulating action is generally due to very large anions and pyrophosphates do not give it.

In these circumstances it is obvious that free metaphosphoric acid can have very varied properties. Indeed, it can be syrupy and hygroscopic, or glassy and very sparingly soluble according to the method of preparation. Up to the present a definite crystalline form is not known.

Just as free metaphosphoric acid can be transformed into ortho-phosphoric by absorption of water, the metaphosphates may also be changed into orthophosphates by taking up metallic oxides: $NaPO_3 + Na_2O \longrightarrow Na_3PO_4$. Coloured orthophosphates formed from metallic oxides are of special interest, and are used for the recognition of the metals in the microcosmic bead. It is not necessary to use the metal as the oxide, but it may be allowed to react in the bead as the salt of an acid which is more easily volatile than phosphoric acid : $NaPO_3 + CuSO_4 \longrightarrow NaCuPO_4 + SO_3$.

These beads normally exhibit the same colour as the ions of the metal in aqueous solution. If the colouring metal exists in several stages of oxidation, the colours of higher ones may be observed by heating in the oxidising flame, and the colours of the lower by heating in the reducing portion. Metals which stand below hydrogen in the electromotive series are often converted in the reducing flame to the metal which then colours the bead. The following colorations

are obtained (the Roman numerals denote the valency of the metal which colours the bead):

	Fe	Ni	Co	Mn	Cr
Oxidising flame	Brown (III)	Green (II)	Blue (II)	Violet (III)	Green (III).
Reducing flame	Bright green (II)	Grey (Met.)	Grey (Met.)	Colourless (II)	Green (III).
	Cu	Mo	W	V	Ti
Oxidising flame	Greenish blue (II)	Colourless (VI)	Colourless (VI)	Colourless (V)	Colourless (IV).
Reducing flame	Reddish brown (Met.)	Blue (IV)	Blue (IV)	Green (III)	Violet (III).

Perphosphoric Acids.—Acids of phosphorus are known which correspond to Caro's acid and to perdisulphuric acid:

$$OP{\displaystyle{\diagup{(OH)_2} \atop \diagdown{O.OH}}} \qquad \text{and} \qquad (HO)_2:P{\displaystyle{\diagup{O \quad O} \atop \diagdown{O-O}}}P:(OH)_2$$

Permonophosphoric acid.   Perdiphosphoric acid.
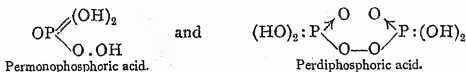
These are formed in a similar way to the sulphur acids—by the addition of H_2O_2 to P_2O_5: $2H_2O_2 + P_2O_5 + H_2O \longrightarrow 2H_3PO_5$, or by the electrolytic oxidation of phosphates,[1] e.g.: $2H_3PO_4 + O \longrightarrow H_4P_2O_8 + H_2O$. Hydrogen peroxide can combine only with P_2O_5 or its lower hydrates, and the best way of preparing permonophosphoric acid is to carry out the reaction in acetonitrile solution. Orthophosphoric acid does not react with hydrogen peroxide. If P_2O_5 is used as the initial substance it is possible to obtain the acid H_3PO_5 but if pyrophosphoric acid is used, $H_4P_2O_8$ is formed. The electrical method requires low temperatures and a small current density (in which it differs from perdisulphuric acid) as well as the avoidance of cathode reduction, which is obtained by the addition of chromate (cf. p. 370); the presence of fluoride is also advantageous.

Permonophosphoric acid is distinguished by its ability to oxidise manganous compounds direct to permanganates. The precipitate produced with silver salts is also characteristic: after the initial dark precipitate the deposit becomes white very rapidly (Ag_3PO_5), and then forms yellow Ag_3PO_4, with gradual evolution of ozonised oxygen. Other heavy metal salts also give easily decomposed deposits, but solid alkali salts of the acid have not been prepared. By the action of hydrogen peroxide on sodium phosphate a salt is obtained with a strong oxidising action, but it contains no higher phosphoric acid; the hydrogen peroxide is linked on as an entire molecule, as in certain percarbonates, perborates, etc., in which it replaces a portion of the water of crystallisation in the phosphate. Such compounds are completely split up in aqueous solution, and show only the behaviour of free H_2O_2 and not that of the oxidised salt,

[1] Schmidlin and Massini, Ber., 1910, 43, 1162; Fichter and Müller, Helv. Chim. Acta, 1918, 1, 297; Toennies, J. Amer. Chem. Soc., 1937, 59, 555.

while the true per-acids retain their special reactions in solution and decompose only gradually on hydrolysis:

$$OP\!\!\diagup^{(OH)_2}_{\diagdown O.OH} + H_2O = OP\!\!\diagup^{(OH)_2}_{\diagdown OH} + HO.OH.$$
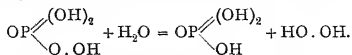
The Acids of Arsenic and Antimony.—Salts of the following acids are known:

H_3AsO_3 arsenious acid	H_3AsO_4 arsenic acid
H_3SbO_3 antimonious acid	H_3SbO_4 antimonic acid.

The formulae of these acids are comparable with those of phosphorous acid, H_3PO_3, and phosphoric acid, H_3PO_4, though analogy in properties is shown only between arsenic acid and phosphoric acid; arsenic acid is obtainable in the free condition, but the others all decompose so easily into their anhydrides and water that the solid acid hydrates remain unknown. Hydrated antimony trioxide and pentoxide are formed when the salts are precipitated with a suitable quantity of a strong acid, but they are only colloidal precipitates, which contain the water more or less firmly adsorbed. The "compound" H_3SbO_3, is a white precipitate, and is dehydrated on standing under water, when it is converted to Sb_2O_3. "**Antimonic acid,**" H_3SbO_4, which is also quite amorphous, gives opalescent translucent lumps when partly dried, which fall to a powder on being dried further; this compound does not correspond to a definite hydrate any more than silicic acid. It retains some water at 200°, but many colloids behave in this way and the water is not part of the constitutional formula. Antimonic acid also resembles silicic and stannic acids in other properties: it is almost insoluble in acids and alkalis, and even with strong bases like caustic potash it does not form an antimoniate. When obtained by the hydrolysis of $SbCl_5$ it forms a completely clear solution which coagulates on heating. The "acid" also separates on the addition of H˙ or OH′ ions, but goes into solution again after the electrolyte has been entirely removed by washing. If it is prepared by the oxidation of tervalent antimony compounds with nitric acid it is obtained at once in large particles, which do not give a clear (pseudo) solution after being washed with water, but only a turbid suspension; when prepared by the action of *aqua regia* on metallic antimony the dehydration and polymerisation process may go so far that the precipitate separating from the original solution is absolutely insoluble, like certain forms of stannic acid. There is even less evidence for the existence of a true hydrated antimonious acid, H_3SbO_3.

On the other hand, it is probable that **arsenious acid** exists in solution, but to a very limited degree since it decomposes with great ease into its anhydride, As_2O_3, and water. This anhydride is, however, somewhat soluble in water and the solution has a weakly acid reaction.

When investigated by the hydrolysis method its acidity is found to be less than that of hydrogen sulphide, but greater than that of boric acid. Its salts, of which only those of the alkalis are soluble, are so strongly hydrolysed that they may be titrated by acids like free alkali.

Arsenic acid is the only acid of this group which can be isolated; it is also the strongest (*cf.* p. 718). It is obtained by the oxidation of elementary arsenic or arsenic trioxide with nitric acid, *aqua regia*, chlorine water, etc. Atmospheric oxygen oxidises alkaline arsenite solutions to arsenate, but only very slowly. Arsenic acid is easily and permanently soluble in water; it crystallises on concentration in small needles with the ortho-formula H_3AsO_4, if the evaporation is carried out at $100°$. If evaporated at a lower temperature it forms clear, moderately hygroscopic plates melting at $36°$, with the composition $2H_3AsO_4, H_2O$. They are isomorphous with the hydrate of phosphoric acid, $2H_3PO_4, H_2O$. This isomorphism is found not only in the free acids, but in the salts as well; Mitscherlich discovered the law of isomorphism by comparing phosphates with arsenates. The properties of arsenates and phosphates are very similar. Thus the arsenates include imperfectly crystallised and anhydrous potassium salts, well-defined sodium compounds with 7 and 12 H_2O, the primary, secondary and tertiary forms, and the sesqui-salts, *e.g.* $Na_3H_3(AsO_4)_2, 3H_2O$. Just as in the phosphates, only the tertiary alkali salts and that of univalent thallium are soluble in water; the others separate first as amorphous precipitates which afterwards become crystalline. These precipitates, like the phosphates, dissolve in weak acids, and with excess arsenic acid form secondary and primary salts of much greater crystallising power and solubility. The same types of precipitates are characteristic for both: the yellow precipitate of ammonium arsenomolybdate is formed under the same conditions as the phosphomolybdate, and has a similar external form; magnesium ammonium arsenate, $Mg(NH_4)AsO_4$, corresponding to the phosphate, $Mg(NH_4)PO_4$, is similarly sparingly soluble in ammonia and has similar crystals shaped like coffin lids. Whereas silver phosphate is yellow, the arsenate is chocolate brown; it is always precipitated in the tertiary form as Ag_3AsO_4, so that if a primary arsenate is precipitated the free acid remains in solution. There is an essential difference at only one point: while the conversion from the orthophosphates to pyro- and meta-phosphates by the elimination of water takes place only at higher temperatures, it is completed in the arsenates with much greater ease. The aqueous solution of the metarsenate, $KAsO_3$, and of the acid orthoarsenate, KH_2AsO_4, *i.e.* $KAsO_3 + H_2O$, are not in the least different from each other, *e.g.* they have exactly the same conductivity. The same is true of the solutions of secondary orthoarsenate Na_2HAsO_4, *i.e.* $Na_4As_2O_7 + H_2O$, and of sodium pyroarsenate, $Na_4As_2O_7$. The con-

sequence of this extremely easy mutual conversion of the hydrated forms is that the heavy metal arsenates obtained by precipitation belong sometimes to one type and sometimes to another.

This property is found in the other acids of this group, and is highly developed, for instance in the **arsenites**, where besides salts of the ortho-acid, H_3AsO_3, those of the meta-acid, $HAsO_2$, of the pyro-acid, $H_4As_2O_5$, and even some apparently derived from other stages of hydration, such as $H_2O . 2As_2O_3$ or $2H_2O . 3As_2O_3$, also exist. The following list gives the formulae of some arsenites which are formed by precipitating $NaAsO_2$ solutions with heavy metal salts:

$$Ni_3As_2O_6 \qquad Pb_3As_2O_6 \qquad Zn_3As_2O_6 \qquad Co_3As_2O_5 \qquad Cd_2As_2O_5$$
$$Cu_4As_2O_7 \qquad Fe_4As_2O_7 \qquad Mn_5As_2O_8 \qquad Hg_5As_2O_8 \qquad Ag_6As_2O_9 \qquad \text{etc.}$$
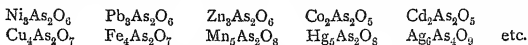
The investigation of these salts is made difficult by the adsorption of As_2O_3 by the metallic hydroxide; this is especially marked in $Fe(OH)_3$, so that precipitated ferric hydroxide is given as an antidote in arsenical poisoning. A compound of the hydroxide and arsenic trioxide is not formed, but the association takes place entirely by surface action, as may be confirmed by distribution experiments.[1] Most of these arsenites are not precipitated by merely bringing the alkali arsenite and the heavy metal salt together, but remain in solution, and the precipitate appears only on the addition of alkali hydroxide. Bright yellow silver arsenite, Ag_3AsO_3, the white lead salt, $Pb_3(AsO_3)_2$, and the copper salt, $Cu_2As_2O_5$ (Scheele's green), are most characteristic, the last (like the first) being soluble in excess alkali. The green solution thus obtained, which contains a cupric arsenite complex, separates in time with the reduction of the cupric ion; for arsenious acid, like phosphorous acid, reduces the salts of the more noble metals, and precipitates metallic gold from auric salts and grey mercury from mercuric salts. The arsenites of the alkali metals decompose on heating like the phosphites, into arsenate and elementary arsenic.

The **antimonites** show exactly similar variations in the forms of the salts: from salts of the acid, $HSbO_2$, precipitation gives salts of such acids as $HSb_3O_5 \longrightarrow H_2O . 3Sb_2O_3$; $H_2Sb_4O_7 \longrightarrow H_2O . 2Sb_2O_3$; $H_4Sb_6O_{11} \longrightarrow 2H_2O . 3Sb_2O_3$; $H_2Sb_{10}O_{25} \longrightarrow H_2O . 8Sb_2O_3$, etc.—combinations of the most diverse proportions of bases and Sb_2O_3. The alkali antimonites are more highly hydrolysed than the arsenites, so that they are decomposed by water with the deposition of solid Sb_2O_3 and are soluble only in excess alkali. The composition of solid antimonites is dependent to a large extent on the temperature of preparation as well as on the excess of base. The isolated alkali salts are mainly metantimonites, e.g. $NaSbO_2$.

The **antimonates** are very similar to the antimonites, but the formation of salts of the meta-acid $HSbO_3$ is most common. The

[1] W. Biltz, *Ber.*, 1904, 37, 3138.

decrease in the acid strength from phosphoric to arsenic acid leads one to expect a further decrease in antimonic acid. Here even the primary salts react strongly alkaline. Of the secondary salts, those of the alkalis, to which the pyro-formulae $K_2H_2Sb_2O_7$ and $Na_2H_2Sb_2O_7$ are given, are noteworthy, since they do not lose their water even at 350°. The potassium salt is distinguished by its crystalline form; the sodium salt is soluble in water only to the extent of 0·31 g. per litre at 12°, so that it may be used in the detection of that metal. Many salts of antimonic acid are probably derived from more polymerised forms of the acids, such as tri- or tetra-antimonic acids. The arsenates and antimonates, like the phosphates, are very resistant to dry heating.

Antimony and arsenic form thio- and chloro-acids more readily than phosphorus. These acids, in which the oxygen of the arsenic and antimonic acids is exchanged for sulphur or halogen, are referred to on pp. 737 and 756.

Bismuthic Acid.—The acid character of the hydroxyl compound diminishes continuously with increasing atomic weight from nitrogen to antimony, while the basic properties increase. In tervalent bismuth this tendency has already reached a stage when $Bi(OH)_3$ is no longer able to give H· ions, but functions exclusively as a base; in its higher valency also, the acid character is much diminished in bismuth. A hydrated bismuthic acid, $HBiO_3$, exists even less than free antimonic acid, and it is immediately decomposed into the anhydride and water, which may remain adsorbed. The alkali salts of this acid are obtained as deep reddish-brown substances, approximating to $KBiO_3$ and $NaBiO_3$ in composition; these are prepared by the oxidation of $Bi(OH)_3$ suspended in alkali, by chlorine or at the anode. These alkali salts are certainly not pure, for they undergo hydrolysis like the antimonites, and are also partially reduced to bismuth compounds of lower valency, part of the base remaining adsorbed on the hydroxide. It is even possible that the bismuthates are merely bismuth pentoxide on which alkali hydroxide is adsorbed, and the insolubility of the compounds may be quoted in support of this view. As oxidising agents they are powerful and useful, e.g. in oxidising manganese salts to the permanganate stage in approximately $3N$ nitric acid solution.

SULPHUR AND HALOGEN COMPOUNDS OF THE ELEMENTS OF THE FIFTH GROUP

Nitrogen sulphides—Sulphides of P, As and Sb—Nitrogen halides—Halogen compounds of P, As, Sb and Bi—Oxy- and thio-halogen compounds

Sulphur Compounds

ALTHOUGH the oxygen compounds of nitrogen differ in many ways from those of phosphorus, arsenic and antimony, a comparison between the sulphur compounds of nitrogen and those of the heavier elements of this group can be made with advantage.

Nitrogen Sulphide and Related Substances

An extensive series of compounds of sulphur and nitrogen exists, if those containing halogen as well are included; their formulae are remarkable, but their constitutions still await explanation. The most simple and most thoroughly investigated of them is nitrogen sulphide, N_4S_4, which seems to be formed whenever sulphur reacts with ammonia in the absence of water. Thus it is obtained from a solution of sulphur in liquid ammonia:

$$10S + 4NH_3 \rightleftharpoons 6H_2S + N_4S_4,$$
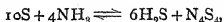
but this reaction is reversible, and if it is desired to prepare nitrogen sulphide by it the hydrogen sulphide must be removed from the equilibrium mixture by the addition of a metallic salt which yields a sulphide (AgI). N_4S_4 is formed in the same way when a suitable compound is decomposed by ammonia with deposition of sulphur. Thionyl chloride, $SOCl_2$, and sulphur chloride, by the action of anhydrous ammonia, first deposit sulphur, which then reacts with the ammonia to yield N_4S_4. Here the H_2S formed is removed by the excess sulphur chloride.

The formula, N_4S_4, for nitrogen sulphide is found by molecular weight determinations, which are made possible by the solubility of the substance in organic solvents. It may also be separated from admixed sulphur in this way, as the latter is sparingly soluble. N_4S_4 crystallises on cooling from the hot solvent in golden yellow crystals, which darken to deep red on heating. They may be sublimed, and melt at 179°; the liquid can be distilled, but since nitrogen sulphide is endothermic it easily explodes. Nitrogen sulphide may, however,

be burnt without explosion, but on percussion a most violent explosion often occurs.

Nitrogen sulphide is decomposed only slowly by water, as it is not wetted by it; the gradual decomposition leads to the formation of various sulphur acids. Sodium hydroxide reacts fairly smoothly as follows:

$$N_4S_4 + 6NaOH + 3H_2O \longrightarrow Na_2S_2O_3 + 2Na_2SO_3 + 4NH_3.$$
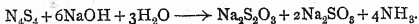
It is easily decomposed by hydrogen chloride, when all the nitrogen splits off as ammonia and the remaining sulphur unites with the chlorine set free: $N_4S_4 + 12HCl \longrightarrow 4NH_3 + (4S + 12Cl)$. The hydrogen chloride is first taken up with the formation of a solid mass, and the nitrogen sulphide here shows its unsaturated character, e.g. it forms with halogens additive compounds which are well-defined crystalline substances, of which N_4S_4, $2Cl_2$ is bright yellow, N_4S_4, $2Br_2$ is bronze, and N_4S_4, $3Br_2$ is dark red. Further, it combines with ammonia to form an orange-red compound, N_4S_4, $2NH_3$, which gives off its ammonia unchanged again at room temperature, but yields interesting metallic salts in liquid ammonia.[1]

Nitrogen sulphide is reduced by stannous chloride to the colourless compound $(HSN)_4$, which is possibly analogous to $(ClSN)_4$. In this substance the hydrogen is directly joined to the sulphur atom, for with formaldehyde it readily forms $(NSCH_2OH)_4$. When treated with sodium hydroxide the reduction product gives off all its nitrogen as ammonia, which indicates that there are not two nitrogen atoms joined together in N_4S_4, otherwise a hydrazine derivative might be expected. The compound $(HSN)_4$ has no acidic properties.[2]

If the nitrogen sulphide is heated in solution it decomposes first to a compound of formula N_2S_5. The bright yellow solution thereby becomes blood red and on evaporation leaves the liquid nitrogen sulphide, N_2S_5, as a deep blood-red oil, which solidifies to grey crystals of melting point 11°, which look and smell like iodine. This compound is somewhat less stable than N_4S_4; it gradually decomposes spontaneously, but may be kept quite well in solution. It explodes on heating.

N_4S_4 undergoes a specially interesting reaction on treatment with sulphur chloride. Pale yellow needles of $[N_8S_4]Cl$ are hereby formed, in which the group $[N_8S_4]$ plays the part of a univalent positive radical similar to ammonium. The compound, however, is probably thionitrososulphonium chloride $(NS)_3SCl$. The same compound is obtained in greater purity by decomposing N_4S_4 with acetyl chloride. The acid radical in it can be replaced by any of the halogens, or by thiocyanate, nitrate or sulphate radicals. All these salts are obtained

[1] Ruff and Geisel, Ber., 1904, 37, 1573.
[2] A. Meuwsen, Ber., 1929, 62, 1959.

by double decomposition of the chloride with the concentrated acid, and form bright yellow crystals, which are quite stable and dissolve in water, in which they are always very soon decomposed, with separation of black-coloured sulphur.[1] Meuwsen[2] considers that these compounds belong to the following series related to SCl_4 :

$$SCl_4, \qquad NS \cdot SCl_3 \qquad (NS)_2Cl_2 \qquad (NS)_2SCl \qquad (NS)_4S.$$
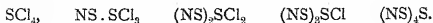
The structure of nitrogen sulphide is not completely elucidated, and it is sometimes formulated as $S : S(: N \cdot S : N)_2$.

Other members of this interesting and puzzling class of compounds may be mentioned :

$(NSCl)_3$, formed by the action of chlorine on N_4S_4,

$S_3N_2Cl_2$, which is formed in brownish crystals from $N_4S_4Cl_2$ and S_2Cl_2, and

$S_6N_4Cl_2$, which is formed as a black crystalline powder with a green metallic lustre by the action of S_2Cl_2 on N_4S_4 in the cold.

Selenium nitride, N_4Se_4, formed by the action of ammonia on selenium monochloride, is an orange yellow, hygroscopic, very explosive, amorphous mass, which is insoluble in water. *Tellurium nitride*, Te_3N_4, is obtained by the interaction of $TeCl_4$ and NH_3.

Sulphur Compounds of Phosphorus, Arsenic and Antimony

The following sulphides are known :

P_4S_3	—	—	P_4S_7	P_2S_5 (P_4S_{10})
As_4S_3	As_4S_4	As_2S_3	—	As_2S_5
—	—	Sb_2S_3	—	Sb_2S_5,
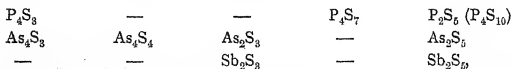
and salts of the following sulphoacids exist :

$$H_3PS_3 \qquad H_3AsS_3 \qquad H_3SbS_3 \qquad H_3PS_4 \qquad H_3AsS_4 \qquad H_3SbS_4.$$

The parent sulphide P_2S_3 of the acid H_3PS_3 does not exist. In these compounds the sulphur may be successively replaced by oxygen, so that one may pass from P_2S_5 to $P_2O_2S_3$ and $P_2O_3S_2$, and from the thioarsenic acids through the following series (*cf.* p. 537) :

$$H_3AsS_4 \qquad H_3AsS_3O \qquad H_3AsS_2O_2 \qquad H_3AsSO_3 \qquad H_3AsO_4.$$
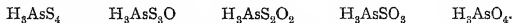
A similar replacement of the sulphur by selenium is also possible. Only the tri- and penta-sulphides correspond to the known oxides, and there is no sulphide corresponding to the oxide of phosphorus, P_8O_{16} (p. 710). Only the tri- and penta-sulphides form thioacids. The sulphides of arsenic and antimony are precipitated by hydrogen sulphide from the ter- or quinque-valent compounds of these elements ;

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[1] Demarçay, *Compt. rend.*, 1880, **91**, 1066 ; 1881, **92**, 726 ; Muthmann, *Ber.*, 1896-97, 29-30.

[2] *Ber.*, 1932, **65**, 1724.

the sulphides of phosphorus, and the lower arsenic sulphides, cannot be obtained in this way, but are prepared by heating phosphorus or arsenic with sulphur.

It is remarkable that phosphorus does not react at all with sulphur at low temperatures, nor when both elements are mixed in CS_2 solution. Sulphur mixes with yellow phosphorus which has not been heated, to form a liquid (solution) which has a low melting point, from which mixed crystals of both elements separate. The eutectic which freezes at $9.8°$ contains about 3 atoms of P to 1 atom of S. If, however, the mixture is heated, combination takes place, frequently with explosion, and it is preferable either to dilute it or to use red phosphorus, which reacts more slowly with the sulphur. If iodine is added, the temperature of combination is lowered. Exactly the same results are obtained if, instead of heating the free elements together, compounds are used; the melt of $4P + 3S$ is exactly the same as that of $P_3S_6 + 5P(= 2P_4S_8)$, that of $4P + 10S(= P_4S_{10})$ is identical with that of $P_4S_8 + 7S(= P_4S_{10})$, that of $4P + 7S(= P_4S_7)$ approximates to that of $P_4S_8 + P_4S_{10}$. However, solutions of $P_4S_8 + P_4S_{10}$ give no P_4S_7 at ordinary temperatures, but only when they are heated together above $100°$.

P_4S_8 is very easily soluble in carbon disulphide; P_4S_7, on the other hand, is almost insoluble; molten naphthalene has proved an excellent solvent for this substance. The sulphides may be purified by recrystallisation or by distillation under reduced pressure. They are obtained from solution or from the fused state as well-crystallised substances, often as transparent needles which are yellowish and vary in colour between quite bright yellow and the colour of flowers of sulphur. The pentasulphide appears in two modifications, which probably differ from each other in molecular complexity. The product formed by rapidly cooling the vapour is much lighter in colour and more soluble in carbon disulphide than that obtained in other ways, and as the vapour density corresponds to the formula P_2S_5, the darker form may be the polymer. The molecular weight in solution corresponds to P_4S_{10}. The vapour density of the other sulphides and their molecular weights in solution lead in general to the formulae given in the table on p. 737; further decomposition sets in only at very high temperatures. All these sulphides can therefore be distilled without decomposition; the boiling points of P_4S_7 and P_2S_5 lie remarkably close to each other, as seen from the following table, which also gives the melting points:

	P_4S_3	P_4S_7	P_2S_5	P_4S_{10}
Melting point .	$172°$	$303°$	$284°$	$247-279°$
Boiling point .	$408°$	$523°$	$514°$	——

P_4S_{10} is split into P_2S_5 on melting, and therefore has no definite melting point. On account of their high boiling points, their low

price and the fact that they do not decompose when boiled, these compounds are suitable liquids for high temperature baths.

The sulphides of phosphorus are unchanged in dry air; in damp air P_4S_3 shows a similar luminosity to free phosphorus, but only above 65°. Here also, as with phosphorus, a definite "luminosity pressure" of oxygen is necessary (cf. p. 133). Atmospheric moisture does not attack P_4S_3 to a marked degree, and on this account it is employed as a filling for match-heads, in which it replaces the yellow phosphorus which was previously used. It is not poisonous, but inflames on friction when it is used in admixture with oxidising substances. P_4S_3 is only slowly decomposed by boiling water, more rapidly in the presence of alkali, when phosphorous acid is formed as a product of autoxidation, while hydrogen, phosphine and hydrogen sulphide appear as auto-reduction products. P_2S_5 and P_4S_7 are somewhat more easily attacked by water, and they smell of sulphuretted hydrogen when exposed to the air. If hydrolysed by alkali, the sulphophosphoric acids tabulated on p. 735 are formed.

Arsenic and antimony sulphides may also be obtained by fusing the elements together, but this method is used only for the preparation of the lower sulphides of arsenic. Of these, As_4S_3 is yellow, and crystallises when sublimed *in vacuo*; it is unimportant. As_4S_4 occurs naturally in large quantities as realgar, and is remarkable for its beautiful red colour. It is easily formed by the methods given for the sulphides of phosphorus, and is also obtained from arsenic trioxide and sulphur: $2As_2O_3 + 7S \longrightarrow As_4S_4 + 3SO_2$.

This sulphide, which sublimes without decomposition at high temperatures, gives a vapour similar in colour to chlorine. The As_4S_4 molecule decomposes only at higher temperatures. As_4S_4 shows a resemblance to the sulphides of phosphorus in its insolubility in carbon disulphide and benzene, as well as in its behaviour towards caustic potash, by which it is decomposed into free arsenic and As_2S_3.

There is only an indication of the existence of the lower sulphides of antimony, inasmuch as molten Sb_2S_3 dissolves metallic antimony and molten antimony dissolves the sulphide. If Sb_2S_3 and Sb are melted together, two phases are obtained, of which the sulphide phase contains more antimony at higher temperatures, e.g. 11·28 per cent. at 539° and 21·9 per cent. at 1180°. The antimony separates again on cooling.

Owing to the more metallic character of arsenic and antimony, solutions of their compounds contain positive "metal" ions. Since the sulphides are very sparingly soluble in water, sulphuretted hydrogen precipitates them from these solutions. This precipitation is naturally most difficult in quinquevalent arsenic, since here the quantity of positive $As^{·····}$ ions is at a minimum. Such solutions are therefore not precipitated directly by sulphuretted hydrogen, but either the

sulphuretted hydrogen first reduces the oxygen atoms in the AsO_4''' ions or they are slowly substituted by sulphur; the series of ions AsO_3S''', AsO_2S_2''', $AsOS_3'''$ and AsS_4''' is then formed, and only the last yields H_3AsS_4 with the hydrogen ions, which then breaks up into H_2S and sparingly soluble As_2S_5. For this reason the precipitation of quinquevalent arsenic with sulphuretted hydrogen is always completed very slowly. All these precipitations occur only in acid solution, since in alkaline solution the sulphides remain dissolved as sulphosalts, and in neutral solution colloidal solutions are formed (cf. below).

The colour of the amorphous precipitated arsenic sulphide is egg yellow, and that of the antimony sulphide orange red. This form of Sb_2S_3 is not the stable one, but in the presence of certain reagents, and even in water on heating to 200°-250°, it changes to the stable form which is greyish black, denser, crystalline and identical with natural stibnite. A vermilion amorphous mass can be obtained from it only by rapidly cooling the vapour. By rapidly cooling the melt, violet forms are obtained which consist of mixtures of the two forms. Sb_2S_5, antimony pentasulphide, and As_2S_5 are known only in the amorphous state; yellow As_2S_3 changes at higher temperatures to a crystalline form, but its colour is not appreciably altered. The crystalline form is identical with naturally occurring orpiment.

The sulphides of arsenic and antimony are not soluble in carbon disulphide, and are not decomposed at all by water. They melt very easily, Sb_2S_3 with most difficulty (550°), and the trisulphides boil at temperatures above 700° without decomposition, while the penta-sulphides decompose at low temperatures into sulphur and the trisulphides; Sb_2S_5 yields two atoms of sulphur on heating in a stream of carbon dioxide at 200°.

The trisulphides are distinguished by a great tendency to occur and remain in the colloidal state. They form very good material for the study of this state, and a series of fundamental colloidal investigations carried out with them served as the foundation for the " valency rule " (p. 101). The variation in the size of the particles, the adsorption of equivalent quantities of cations in coagulation and many other typical properties have also been investigated.[1]

Colloidal As_2S_3 solution is obtained by the action of sulphuretted hydrogen on a solution of As_2O_3; by dissolving more As_2O_3 and repeating the treatment with sulphuretted hydrogen the concentration may be considerably increased; it can be heated to boiling without precipitating, and any excess of sulphuretted hydrogen can be driven off in this way. Solutions with a 37·5 per cent. As_2S_3 content have been obtained, but it is not possible to prepare antimony trisulphide solutions of this strength; they are best obtained by passing sulphuretted hydrogen into dilute solutions of tartar emetic, with subsequent dialysis. They withstand the action of electrolytes much better than arsenic sulphide solution under otherwise similar conditions. They form somewhat larger particles than the latter and are completely

[1] Schultze, *J. prakt. Chem.*, 1882 (2), **25**, 431 ; Linder and Picton, *J. Chem. Soc.*, 1892, **61**, 114 ; 1895, **67**, 63.

retained by the membrane on dialysis, while the finest As_2S_3 solutions even pass through filter candles. Particles of all possible sizes, especially of As_2S_3, may be prepared by using different concentrations for precipitation, and it is characteristic that subsequent dilution of an initially concentrated solution of As_2S_3 does not give the same solution as is obtained by starting with a dilute solution; the size of the particles is different in the two solutions and does not change in the subsequent dilution.

Antimony trisulphide sol is an intense orange red, and its coloration is still visible in a dilution of 1 : 1,000,000. The colour of arsenic trisulphide is yellowish red in very concentrated solution, but otherwise pure yellow, and about ten times weaker than that of Sb_2S_3. As is generally found with colloidal sulphides, both are negatively charged.

The tri- and penta-sulphides of phosphorus, arsenic and antimony combine with metallic sulphides to yield sulphosalts (thiosalts),[1] and with metallic oxides to give oxysulphosalts. The arsenic and antimony compounds of this class do not differ from the sulphosalts of other metals in principle, and have therefore been considered already on p. 537. On the other hand, the corresponding phosphorus compounds differ from the metallic sulphosalts in the great ease with which they exchange the sulphur atoms for oxygen, even by the action of water. A series may be constructed as for the arsenic compounds, but there is a greater tendency for the formation of salts poor in sulphur

$$Na_3PS_4 \qquad Na_3PS_3O \qquad Na_3PS_2O_2 \qquad Na_3PSO_3 \qquad Na_3PO_4.$$
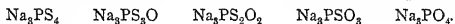
In the presence of water a phosphorus sulphosalt undergoes decomposition in the sense: $2Na_3PS_4 \rightleftharpoons 3Na_2S + P_2S_5$, which proceeds according to the top arrow on dilution, but is reversed on the addition of excess alkali sulphide. For this reason such sulphosalts can be crystallised from solution only in the presence of a large excess of alkali sulphide; since, if P_2S_5 is formed, it is soon decomposed by the water into H_2S and P_2O_5, when the H_2S easily escapes; in this way the whole of the sulphosalt is destroyed. The sulphophosphates of the heavy metals[2] are much more stable to water and are not obtainable from solution but by melting together P_2S_5 and metallic sulphides; in spite of their sparing solubility they are very well defined, melt without decomposition and are crystalline; they are decomposed by acids. The chlorides are used with advantage, instead of the sulphides, in their preparation: $3M^ICl + P_2S_5 \longrightarrow M^I_3PS_4 + PSCl_3$. Sulphohypophosphates $M_4P_2S_6$ and sulphophosphites M_3PS_3 are also known, especially those of the heavy metals, and form well-crystallised, coloured compounds, which separate from a melt prepared from the calculated quantities of metal, sulphur and phosphorus. The alkali sulphophosphites are also obtained from aqueous solution by decomposing P_4S_3 or P_4S_7 with an alkali sulphide, when hydrogen and phosphine are simultaneously evolved. It is noteworthy that here the sulphophosphorous acid occurs as a tribasic

[1] See H. Wünschendorff, *Bull. Soc. chim.*, 1929 [iv.], 45.

[2] Glatzel, *Z. anorg. Chem.*, 1904, 44, 65.

acid, while phosphorous acid, H_3PO_3, contains a non - replaceable hydrogen atom.

<small>Seleno-compounds analogous to most of the thio-compounds mentioned also exist. The water-soluble ones, however, are even more prone to form oxyseleno-compounds.</small>

Two **oxysulphides** of phosphorus are derived from P_2O_5 by partial replacement of the oxygen by sulphur. The compound $P_2O_3S_2$ (of double molecular weight in the state of vapour) is obtained by the direct addition of sulphur to P_2O_3 on heating. It forms colourless prisms which melt at 102° and boil at 295° without decomposition, are easily soluble in carbon disulphide, and are decomposed by water and even by atmospheric moisture, liberating H_2S. The other oxysulphide $P_2O_2S_3$ is formed thus: $2POCl_3 + 3H_2S \Longrightarrow P_2O_2S_3 + 6HCl$. It is partly amorphous and partly needle-like crystals melting at 300° and decomposing on further heating.

Bismuth sulphide (*cf.* p. 528) has the character of a metallic sulphide; it forms no thio-salts.

Halogen Compounds of Nitrogen, Arsenic, Antimony and Bismuth

The nitrogen compounds, which are endothermic with the exception of NF_3, are quite different from the halogen compounds of the remaining elements. For this reason they are considered separately.

Compounds of Nitrogen with the Halogens

The chief derivatives are chlorine and iodine azides (triazochloride and iodide respectively), N_3Cl and N_3I, which have already been considered on p. 663, together with those compounds which are obtained by partial or complete substitution of the hydrogen in ammonia by halogen:

NH_2Cl monochloramine		NF_3	nitrogen trifluoride
NH_2Br monobromamine		NCl_3	nitrogen trichloride
NHI_2 (?)	$N_2H_3I_3$	NI_3	nitrogen tri-iodide.

There is also evidence for NH_2F and the series NHF_2, $NHCl_2$ and $NHBr_2$; and Schmeisser[1] has prepared $NBr_3,6NH_3$.

Further, compounds are formed by the addition of 1, 2, 3 and 12 molecules of ammonia to nitrogen tri-iodide, of which $NI_3.NH_3$, the $N_2H_3I_3$ mentioned above, is best known.

The fluorine compound (see p. 744) differs a great deal from those of chlorine and iodine. The latter are formed whenever halogen and ammonia or ammonium salts meet in aqueous solution, preferably when hypochlorite is employed instead of halogen; then, as is well known, ammonia may also be oxidised by the hypochlorite to free

[1] *Naturwiss*, 1940, **28**, 63.

nitrogen (p. 177). The reaction with hypobromite follows this course exclusively. The formation of nitrogen halides may be supposed to take place by the halogen replacing the hydrogen atoms of ammonia directly; but there are advantages in considering that it is not the free halogen, but the hypohalite present in the solution which reacts: $Cl_2 + H_2O \rightleftharpoons HClO + HCl$; the nitrogen halide may be reconverted to hypohalite and ammonia on hydrolysis, so that the formation of nitrogen halide may be referred to the reversible reactions: $NH_3 + 3HOCl \rightleftharpoons NCl_3 + 3H_2O$, or $NH_3 + HOI \rightleftharpoons NH_2I + H_2O$. It seems possible, in view of the low stability of nitrogen bromide, that the reaction in nitrogen chloride takes a different course from that in nitrogen iodide. It is of interest that in the action of iodine on concentrated ammonium iodide solution, ammonium polyiodide (p. 243) and not nitrogen iodide is formed, and that in the presence of the iodides of bivalent metals free ammonia also gives with iodine no nitrogen iodide, but polyiodides of the metallic ammines, *e.g.* $[Ni(NH_3)_6]I_2$.

The product is richer or poorer in halogen, according to the quantity of ammonia used; if the pH of the solution is smaller than 4·4, NCl_3 is formed; between 4·5 and 5·0, $NHCl_2$ is the product, and if it is greater than 8·5 only NH_2Cl is obtained[1]:

$$NH_3 + NaOCl \longrightarrow NH_2Cl + NaOH \qquad NH_3 + 3NaOCl \longrightarrow NCl_3 + 3NaOH.$$
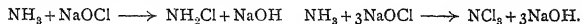
NH_2Br and $NHBr_2$ are obtained in anhydrous ethereal solution from bromine and ammonia; they form primary and secondary amines respectively in comparatively small yields with Grignard reagents.[2]

The addition of iodine to ammonia is best carried out in alcoholic or potassium iodide solution. The product which first separates out is then mainly of the approximate composition $NH_3 . NI_3$, but appears to come nearer to the composition NI_3 on washing with water. NI_3 is best prepared by the action of dry ammonia on the less stable dibromiodides, *e.g.* $3KIBr_2 + 4NH_3 \longrightarrow 3KBr + 3NH_4Br + NI_3$, the resulting salts being washed out with water.[3]

The preparation of very small amounts of nitrogen chloride NCl_3 can be carried out with advantage by the electrolysis of a concentrated solution of ammonium chloride; the chlorine which separates at the anode reacts immediately with the ammonium salt there present. To obtain chloramine, NH_2Cl, hypochlorite is added to the calculated quantity of ammonia, when the chloramine remains in the aqueous solution and may be driven off by distillation *in vacuo*, and so concentrated up to a 12 per cent. solution; on dehydration with potassium carbonate the chloramine is left as a colourless oil, giving crystals on

[1] Chapin, *J. Amer. Chem. Soc.*, 1929, 51, 2112.
[2] Moldenhauer and Burger, *Ber.*, 1929, 62 [B], 1615 ; Coleman, Yager and Sorovs, *J. Amer. Chem. Soc.*, 1934, 56, 965.
[3] Cremer and Duncan, *J. Chem. Soc.*, 1930, 2750.

cooling (m.pt. −66°). Its smell is intermediate between that of NH_3 and NCl_3.

NCl_3 is a bright yellow oil with a powerful, irritating odour; the vapour attacks the eyes in particular. Nitrogen iodide, on the other hand, is solid and amorphous, with only a faint smell. It is sometimes obtained in needles which recall the dichroic colours of the polyiodides —red in transmitted light, in reflected light coppery black. With great care NCl_3 may be distilled; it boils below 71°; at −40° the oil is not frozen.

These compounds are very highly explosive. Nitrogen chloride explodes on contact with reagents which it can chlorinate immediately, and also on heating alone to 95°. Nitrogen iodide explodes violently without any visible external impetus. Particularly in the dry condition, a slight touch or strong illumination by a magnesium light is sufficient to cause it to decompose. It explodes in 20 sec. under the action of the α-rays of radium of 3 millicurie concentration at 1 cm. distance. Like NCl_3, it decomposes gradually in diffused light, and also slowly under water with evolution of nitrogen. In benzene solution in the dark, NCl_3 may be kept for a time.

Chloramine and bromamine are soluble in water, but the others are insoluble; the nitrogen iodides rich in ammonia gradually lose ammonia on washing and form NHI_2, and perhaps products richer in iodine. NCl_3 dissolves very well in benzene, carbon disulphide, chloroform, sulphur chloride and similar solvents, without undergoing decomposition. Chloramine decomposes slowly in aqueous solution, as follows, if H· ions are continuously removed: $3NH_2Cl \longrightarrow NH_4Cl + 2HCl + N_2$. Double decomposition takes place with hydrochloric acid; e.g.: $NHI_2 + 2HCl \longrightarrow NH_3 + 2ICl$, likewise with ammonia: $NCl_3 + NH_3 \longrightarrow N_2 + 3HCl$; the reaction between chloramine and ammonia (but not that of bromamine) can be stopped at the intermediate stage of formation of hydrazine (cf. p. 653).

Nitrogen iodide, on the other hand, combines with gaseous ammonia in the cold, and at −60° the compound NI_3, $12NH_3$ is formed; at temperatures somewhat below room temperature ammines with 2 and 3 mols. of ammonia may be formed, which lose ammonia in vacuo, but only to the stage NH_3, NI_3. If one tries to remove the last ammonia molecule complete decomposition ensues.

Nitrogen trifluoride is very different, both in formation and properties from the foregoing compounds. It has been studied by Ruff, Fischer and Luft,[1] and, although it can be made by the direct union of the two elements, or by the replacement of the chlorine in nitrogen trichloride by fluorine, the best method is the electrolysis of ammonium bifluoride; small amounts of NH_2F and NHF_2 are formed simultaneously. NF_3 is a colourless gas which condenses to a

colourless liquid at $-119°$ and freezes at $-216\cdot6°$. It is much more stable than the other nitrogen halides and is non-explosive; like sulphur hexafluoride, it does not attack dry glass. It does not react with water or even with caustic alkalis. When an electric spark is sent through a mixture of this gas with water vapour, brown fumes and a blue flame appear in consequence of the reaction: $2NF_3 + 3H_2O \longrightarrow 6HF + N_2O_3$. Hydrogen reacts also when the mixed gases are sparked, nitrogen and hydrogen fluoride being formed with violent explosion: $2NF_3 + 3H_2 \longrightarrow N_2 + 6HF + 336$ Cals.

Halogen Compounds of P, As, Sb and Bi

Composition.—The chief type of these compounds is the trihalide. All the sixteen possible compounds of the type MX_3, as well as certain mixed halides:

$$PF_2Cl \qquad PFCl_2 \qquad PF_2Br \qquad PFBr_2$$
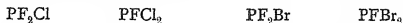
some compounds with smaller halogen content, exist:

$$P_2Cl_4 \qquad P_2I_4 \qquad As_2I_4 \qquad Bi_2Cl_4 \qquad Bi_2Br_4.$$
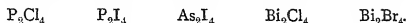
Similar compounds of antimony are unknown. Some trihalides are able to take up still larger quantities of halogen. Of the pentahalides thereby formed, the following only are known:

$$PF_5 \qquad AsF_5 \qquad SbF_5 \qquad PCl_5 \qquad SbCl_5 \qquad PBr_5.$$

$SbBr_5$ and BiF_5 have not been isolated, but exist at least in the form of their halogeno-acids $HSbBr_6$ and $HBiF_6$. The halogeno-acids of quadrivalent antimony are likewise known: H_2SbCl_6 and H_2SbBr_6.

Halogen compounds of phosphorus and antimony with more than five halogen atoms, mostly of different kinds, also exist, *e.g.*:

$$PCl_5Br_4 \qquad PCl_3Br_8 \qquad PCl_2Br_7 \qquad PBr_7 \qquad SbCl_7I_2.$$

Thus, while the group of trihalides is complete and regular, the cause of the stability of the other halogen compounds is far from clear. Fluorine alone seems to be especially favoured in the pentahalides, while in the dihalides no fluorine compounds are known, but this is possibly due to lack of experimental data. Regular stages in stability are most clearly shown in the pentahalides of phosphorus, which have limits of existence which become increasingly smaller as the atomic weight of the halogen increases; PF_5 is very stable, but it has not been possible to obtain PI_5. The addition to a central atom takes place with more difficulty the larger the volume of the portion to be added. According to Pauling, hybridisation

of the bond orbitals could lead to a completely covalent structure, *e.g.*

$$F—P \begin{matrix} F \\ F \\ F \\ F \end{matrix}$$
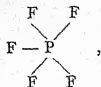
, but such a structure is of minor significance only. The molecule is a resonance hybrid, the resonating structures containing at most four covalencies, as in

$$\overset{..}{\underset{..}{:F:}}^{-} \overset{+}{\underset{\underset{F}{|}}{P}} \overset{F}{\diagdown_{F}}$$
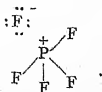
With the pentabromide, in which the elements are more similar in electronegativity, the five covalent structure may be more important. PCl_5 may certainly be regarded as a derivative of quinquevalent phosphorus, but it can also be considered as a secondary valency compound, $PCl_3 \cdot Cl_2$. Moreover, the fact that compounds also exist with more than five halogen atoms (*cf.* the bromine addition products of PCl_3), in which one can hardly assume that the phosphorus has a valency greater than five, shows definitely that supplementary valency compounds occur in this group; these compounds may, however, be related in type to the interhalogen compounds (see p. 387).

Various other electronic formulae have been put forward for pentahalides of this group, *e.g.*
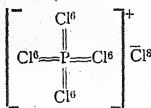
I. II. III.

This type of formula could not be used, for example, for PCl_3Br_2, which would involve a valency shell of 22 electrons. Other formulae suggested for the pentahalides are the polar type II, and one containing singlet linkages III. Against II is the fact that PCl_5 is a non-polar material; it is non-conducting and has a very small dipole moment. Formula III certainly shows two chlorine atoms combined in a way different from the others, and phosphorus is shown with an octet; parachor measurements agree with this formulation, but by adopting a different method of calculation, support can be found for the penta-covalent formula I. These remarks indicate the value of the concept of resonance in interpreting the properties of compounds of this sort. The crystal structure of PCl_5 shows a tetragonal unit cell of 4 P and 20 Cl atoms arranged as PCl_4^+ and PCl_6^- ions in a distorted C_5Cl lattice.

Formation.—The halogen compounds of this group are all formed in the same way, namely by direct union of the halogen with the central element. If the halogen is in excess, compounds rich in halogen are formed; if not, those poorer in halogen:

$$P + I_2 \longrightarrow PI_2 \qquad\qquad 2P + 3I_2 \longrightarrow 2PI_3$$
$$2Sb + 3Cl_2 \longrightarrow 2SbCl_3 \qquad 2Sb + 5Cl_2 \longrightarrow 2SbCl_5.$$
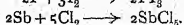
The compounds containing less halogen may be obtained from the more highly halogenated ones by the addition of an excess of the central element; usually it is necessary to heat:

$$2AsI_3 + As \longrightarrow 3AsI_2.$$
$$2BiBr_3 + Bi \longrightarrow 3BiBr_2.$$
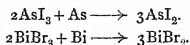
The more highly halogenated compounds can be built up from those with less by the addition of halogen:

$$PCl_3 + Cl_2 = PCl_5 \qquad\qquad PCl_3 + Br_2 = PCl_3Br_2.$$

The addition takes place with great ease, often with incandescence, on passing the vapour of the halogen over the compound. The reaction can also be carried out in solution. Instead of the free central element, its oxide or sulphide may be treated with halogen:

$$Bi_2O_3 + 3Br_2 \longrightarrow 2BiBr_3 + 3O \qquad As_2S_3 + 3Cl_2 \longrightarrow 2AsCl_3 + 3S,$$
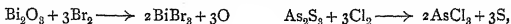
and instead of the free halogen, compounds which are able to yield their halogen easily may be employed, e.g. S_2Cl_2, PCl_5 or $SiCl_4$.

Another method for the preparation of these compounds is by the double decomposition of the oxides or hydroxides with the halogen hydrides, e.g.:

$$Bi(OH)_3 + 3HCl \longrightarrow BiCl_3 + 3H_2O; \; As_2O_3 + 6HBr \longrightarrow 2AsBr_3 + 3H_2O.$$
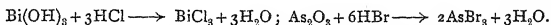
These reactions are reversible; if excess of halogen hydride is not present the oxide, hydroxide, or at least a basic salt, is formed again. The method generally fails with phosphorus, since the hydrolysis equilibrium is very much in favour of the free halogen acid. With the other elements, however, the halogen compounds can be obtained crystalline from the halogen hydride solution of the hydroxide on evaporation if a sufficient excess of the halogen acid is present.

Some of these compounds are obtained by double decomposition with metal halides in the fused state. The fluorine compounds in particular are prepared thus, since free fluorine is not easily obtainable, e.g.:

$$2PBr_3 + 3ZnF_2 \longrightarrow 2PF_3 + 3ZnBr_2; \; As_2O_3 + 3CaF_2 \longrightarrow 2AsF_3 + 3CaO.$$
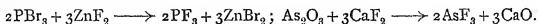
Properties.—The state of aggregation of these compounds is strongly influenced by the kind and quantity of the halogen present. Three of the fluorides are gaseous at the ordinary temperatures (PF_3, PF_5, AsF_5); the iodides are all solid. In the table on p. 748 the upper numbers indicate the melting points, and the lower the boiling points, of the compounds. The gaseous compounds are printed in italic, the liquid in roman, and the solid in heavy type; the coloured ones are indicated by * (for mixed halides see p. 751). The fluorides of this group are al colourless, the iodides all yellow or red, BiI_3 being brownish black. SbI_3 exists in three different forms: the normal trigonal form is red,

and when it is sublimed a greenish yellow, rhombic form is produced, which is suddenly transformed into the red form at 114°. A monoclinic modification, also greenish yellow, separates when solutions of red SbI_3 are exposed to light, and is reconverted to this variety at 125°. The following members of this group are also coloured:

PBr_5	Bi_2Cl_4	Bi_2Br_4	$BiBr_3$.
Orange-yellow and red.	Brownish-black.	Blackish-brown.	Orange.

PBr_5, as has already been mentioned, is dimorphic; the citron yellow

Fluorides.	Chlorides.	Bromides.	Iodides.
—	$P_2Cl_4 \; {-28° \atop 180°}$	—	*$P_2I_4 \; {110° \atop \text{decomp.}}$
$PF_3 \; {-83° \atop -75°}$	$PCl_3 \; {-112° \atop 76°}$	$PBr_3 \; {-41.5° \atop 172°}$	*$PI_3 \; {61° \atop 120° \text{ at 15 mm.}}$
$PF_5 \; {-151.5° \atop -101.15°}$	$PCl_5 \; {148° \atop \text{decomp.}}$	*PBr_5 ?	—.
—	—	—	*$As_2I_4 \; {<150° \atop ?}$
$AsF_3 \; {-38.5° \atop 63.5°}$	$AsCl_3 \; {-18° \atop 130°}$	$AsBr_3 \; {35° \atop 220°}$	*$AsI_3 \; {146° \atop \text{cr. } 400°}$
$AsF_5 \; {-0° \atop -53°}$	—	—	—
$SbF_3 \; {292° \atop 319°}$	$SbCl_3 \; {73° \atop 223°}$	$SbBr_3 \; {90° \atop 280°}$	*$SbI_3 \; {167° \atop 401°}$
$SbF_5 \; {6° \atop 150°}$	$SbCl_5 \; {-6° \atop 102° \text{ at 68 mm.}}$	—	—
BiF_3 ?	*Bi_2Cl_4 ?	*Bi_2Br_4 ?	—
—	$BiCl_3 \; {232° \atop 447°}$	*$BiBr_3 \; {200° \atop 423°}$	*$BiI_3 \; {439° \atop \text{subl.}}$

form is the normal one; the yellow form made by rapidly cooling the vapour is converted to the red one on friction. The intense coloration of Bi_2Cl_4 and Bi_2Br_4 is in good accordance with their tendency to dissociate; oscillations may be assumed to take place in the molecules, thus: $Bi_2Cl_4 \rightleftarrows Bi + BiCl_3$, since wherever such reversible oscillating transpositions are possible deep colours appear. In this group they are also seen in the deep brownish-black compounds of the acids H_2SbCl_6 and H_2SbBr_6, the basic halogen compounds of which, $SbCl_4$ and $SbBr_4$, are unstable and oscillate in the sense $2Sb^{IV} \rightleftarrows Sb^{III} + Sb^{V}$. The very dark cupro-cupric compounds are further examples of the deep colour of substances showing intermediate valency. The black

colour of thallo-thallic salts is explicable from the same standpoint, also that of Fe_3O_4, the deep colour of N_2O_4, etc.

Instead of this oscillation theory, however, it is simpler to assume that the valency electrons are equally divided between two competing atoms. The distribution of electrons is then greatly distorted and incident light of every or almost every wave-length finds a point of attack.

These halides are bad conductors of electricity in the liquid state, but nevertheless some of them conduct noticeably, and those of them which dissolve salts behave as dissociating solvents. $AsCl_3$ and $SbCl_3$ have been specially investigated, and dissolve some metal halides, but the results are not very clear, since double compounds (halogeno-salts) are formed between solvent and solute. For the same reason molecular weight determinations, in which arsenic and antimony halides serve as solvents, can only be used cautiously, e.g. for iodine, which is soluble in $SbCl_5$, and gives black crystalline compounds of the formula $SbCl_5, 2ICl$, and $SbCl_5, 3ICl$ with partial extraction of the chlorine.

The molecular weights of the compounds themselves, as far as they can be obtained in the state of vapour, are always simple. With the exception of the bismuth compounds they are all soluble in benzene or carbon disulphide, and then give the same simple molecular formulae. Bismuth bromide is soluble in ether.

Measurements of the valency angles of PF_3, PCl_3, and $AsCl_3$ by electron diffraction methods, lead in each case to values[1] of approximately 103°.

Hydrolysis.—They are hydrolysed by water, but it is possible to dissolve the chlorides of arsenic, antimony and bismuth in a little water to a clear solution and SbF_5 is very stable. Bismuth salts are completely hydrolysed with separation of the basic salt; hydrolysis of arsenic trichloride does not lead to the basic salt, but direct to As_2O_3, and as this is soluble in a large amount of water a precipitate is formed only in medium quantities of water. The pentahalides are also completely hydrolysed but give no precipitates with water since the acids formed are soluble. Some of the chlorides, like $AsCl_3$, are volatile in steam, so that their solutions may be vaporised without leaving a residue, especially if excess acid is added; others, like those of phosphorus, are so completely hydrolysed that on heating their aqueous solution only halogen hydrides are evolved, and on evaporation the phosphorus acid remains. The hydrolysis stops at an intermediate stage in a third group, and the compounds are synthesised again on evaporation of the water; thus AsI_3, which is completely decomposed in solution, crystallises on evaporation, as it is formed again when the liquid is concentrated. The trifluorides of antimony and bismuth form an interesting exception. The former is certainly deliquescent, but no basic salt

[1] Brockway and Wall, *J. Amer. Chem. Soc.*, 1934, 56, 2373; Pauling and Brockway, *ibid.*, 1935, 57, 2684.

separates from its solution on dilution; the latter is insoluble in water and is generally not decomposed by it. The reason for this behaviour is apparently due to the lack of dissociation of fluorides, which can be shown in many ways, or to the formation of auto-complex compounds, perhaps in conjunction with feeble ionisation.

Hydrolysis by water leads to the complete elimination of halogen, unless its progress is previously impeded by the separation of a sparingly soluble product. Thus the halogen compounds of phosphorus yield the corresponding acids, e.g.:

$$PCl_3 + 3H_2O \longrightarrow P(OH)_3 + 3HCl; \quad PF_5 + 4H_2O \longrightarrow PO(OH)_3 + 5HF.$$
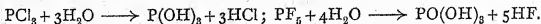
On the other hand, in the compounds of antimony and bismuth it leads to the separation of sparingly soluble oxyhalides:

$$SbBr_3 + H_2O \longrightarrow SbOBr + 2HBr \qquad BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl.$$

Whether the hydrolysis stops at the SbOBr and BiOCl stages naturally depends on the quantity of water employed, and on the temperature; it can also proceed further (cf. p. 754).

In the halides P_2I_4, As_2I_4, Bi_2Cl_4, which correspond to no acid, hydrolysis effects decomposition with simultaneous oxidation and reduction: As_2I_4 or Bi_2Br_4 decompose with the separation of metallic arsenic and bismuth, and the simultaneous formation of tervalent compounds; P_2I_4 decomposes with water, partly with the formation of phosphine, and partly with hydrolysis to HI and H_3PO_3.

These hydrolyses proceed smoothly, but not violently. Even the phosphorus halides which behave most energetically first sink below the water and then only decompose gradually. Phosphorus trichloride yields phosphorous acid only when treated with much cold water. With little water or at higher temperatures other products appear.[1] In the pentahalides the oxyhalides formed as intermediate products can be isolated: $PCl_5 + H_2O = POCl_3 + 2HCl$.

Hydrolysis is also effected by atmospheric moisture. All these compounds therefore fume in air, the extent depending on their vapour pressure. The fumes are only those of the halogen hydride formed on hydrolysis. Phosphorus trifluoride is a noteworthy exception, as it does not fume in air in spite of its gaseous condition. The more easily volatile compounds otherwise give off thick clouds, especially the pentahalides, in which hydrolysis proceeds very quickly; even some of the solid compounds, such as antimony trichloride, fume slightly. The bismuth compounds, on the other hand, do not exhibit this phenomenon.

Dissociation.—Even the trihalogen compounds can act as halogenating agents: e.g. on heating with metals they convert the metal

[1] Wolf, *Ber.*, 1932, **65**, 488.

into its halide. The pentahalogen compounds, however, possess this property to a far greater extent, as they undergo dissociation into free halogen and trihalide ($PBr_5 \rightleftharpoons PBr_3 + Br_2$). At moderate temperatures they act almost as powerfully as free halogen, and at higher temperatures they behave exactly like the halogens. Antimony trifluoride is a widely used fluorinating agent.[1]

The degree of dissociation can be found from the increase in volume as well as from the colour change (*cf.* NO_2, p. 672); for example the position of equilibrium in the reactions $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ can be arrived at by measuring the depth of the green colour, due to free chlorine.

It has already been mentioned that the tendency of the phosphorus pentahalides to dissociate increases with increase in the atomic volume of the halogen (p. 745). Thus PF_5 is stable at high temperatures, while PCl_5 is decomposed thus:

Temperature	182°	200°	250°	274°	300°
Per cent. decomposition	41·7	48·5	80	87·5	97·3

PBr_5 is still more strongly dissociated. PI_5 cannot be prepared. The behaviour of the antimony compounds is similar, but $SbCl_5$ seems to be more stable than PCl_5, though $SbBr_5$, in contrast to PBr_5, cannot be prepared. $AsCl_5$ does not exist above $-40°$.

The halogen added to trihalides may be different from that already present but it is not possible to add on iodine to form a pentahalide. The phosphorus compounds, and to a lesser extent those of antimony, have a special tendency to form pentahalides, but arsenic and bismuth give no mixed halides. The phosphorus compounds are simply obtained by the action of halogens on trihalides:

$$PF_3 + Cl_2 \longrightarrow PF_3Cl_2 \qquad PF_3 + Br_2 \longrightarrow PF_3Br_2.$$

The compounds PCl_3Br_2, PCl_3Br_4, PCl_3Br_8 are formed similarly by the addition of 1, 2 and 4 mols. of bromine to PCl_3. PF_3, PF_2Cl and $PFCl_2$ also react with Cl_2 and with Br_2, but the compounds formed tend to be disproportionate.

The properties of these compounds may be anticipated from those of the simple halides. The fluorides are very stable and easily volatile, the chlorobromides decompose on heating into the chloride and free bromine, and are solids at the ordinary temperature. Their behaviour towards water is like that of the pure pentahalides. The mixed compounds containing fluorine are split up on heating thus:

$$5PF_3Cl_2 \longrightarrow 3PF_5 + 2PCl_5$$
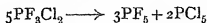
(in this case at 200°, the bromofluoride at 15°). Some properties

of the most important compounds may be seen from the following table :

PF_2Cl	m.pt.	$-164.8°$	b.pt.	$-47.3°$	
$PFCl_2$	,,	$-144°$	,,	$13.9°$	
PF_2Br	,,	$-135.8°$	,,	$-61.1°$	
$PFBr_2$	,,	$-115.0°$	,,	$74.8°$	
PF_3Cl_2.	Colourless gas, becomes liquid at $-8°$.				
PF_3Br_2.	Brownish liquid, yellow crystals at $-20°$.				
PCl_3Br_2.	Yellowish-red crystals decomposed at $35°$.				
PCl_3Br_4.	Ruby-red crystals decomposed at $60°$.				
PCl_3Br_8.	Brown needles with a green lustre, melting point $25°$. May be distilled at $290°$ without decomposition.				
PBr_7.	Is not a mixed halide, but belongs to this class. Forms red crystals.				
PCl_5, ICl.	Orange-yellow crystals.				
$SbCl_3F_2$.	White crystals, melting point $55°$.				
	SbF_2Br, SbF_5I_2 and $(SbF_5)_2I$ are also known.				

Oxy- and Thio-halides.—Some trihalides can also take up additional sulphur or oxygen: $PF_3 + O \longrightarrow POF_3$; $PBr_3 + S \longrightarrow PSBr_3$.

Here again phosphorus shows the greatest tendency to react, while antimony forms only a few such compounds and arsenic and bismuth none at all. The absorption of oxygen, although it is an exothermic process, is very slow and a catalyst or a high temperature is necessary. Thus a mixture of PF_3 and O_2 hardly changes at all in the cold, but if an electric spark is passed, union takes place with explosion; it may be carried out more quietly by leading the gaseous mixture over platinum sponge. PCl_3 also takes up oxygen with difficulty; the addition takes place more quickly if ozone is used. $POBr_3$ may be prepared according to the following reaction :[1]

$$P_2O_5 + 3PBr_5 \longrightarrow 5POBr_3$$
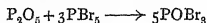
but POI_3 does not exist, though a solid compound of P, I and O has been described; as PBr_5 can be prepared, it is seen that PBr_3 is less able to take up O_2 than Br_2. The addition of sulphur is carried out in the same way. In the cold, and even on moderate heating, it takes place slowly, but more quickly at about $130°$. Not only PF_3 and PCl_3, but also PBr_3 and $SbCl_3$ take up sulphur. The absorption takes place with almost the same vigour as that of bromine.

These compounds are also obtained with advantage by exchanging a portion of the halogen in the pentahalides for oxygen or sulphur by means of H_2O or H_2S :

$$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl \qquad SbCl_5 + H_2S \longrightarrow SbSCl_3 + 2HCl.$$

To moderate the speed and the extent of the reaction, combined water is employed in the form of acids containing water, such as crystallised oxalic or boric acid. Instead of sulphuretted hydrogen, sulphides may also be used with advantage; e.g. PCl_5 gives $PSCl_3$ very

[1] *Inorganic Syntheses*, Vol. II.

conveniently with Sb_2S_3. For the most important of these compounds, $POCl_3$, a special method, the chlorination of P_2O_5, may also be used. This is carried out in such a way that $Ca_3(PO_4)_2$ is acted upon by chlorine at a high temperature, still better in the presence of carbon or carbon dioxide, which permits of the distillation of $POCl_3$ at a moderate heat; possibly phosphorus is formed as an intermediate product, which then yields PCl_5, which with the P_2O_5 gives $POCl_3$.

All these compounds[1] are colourless, except $PSCl_3$ which is lemon yellow. The fluorides are gaseous: $POCl_3$ and $PSCl_3$ are liquid, $PSBr_3$ and $SbSCl_3$ are solid.

	POF_2Cl	$POFCl_2$	$POBr_3$	POF_2Br	$POFBr_2$	PSF_2Cl	$PSFCl_2$
M.pt.	$-96.4°$	$-80.1°$	$45°$	$-84.8°$	$-117.2°$	$-155.2°$	$-96.0°$
B.pt.	$3.1°$	$52.9°$	$195°$	$30.5°$	$110.1°$	$6.3°$	$64.7°$

	POF_3	PSF_3	$POCl_3$	$PSCl_3$	$PSBr_3$	$SbSCl_3$
M.pt.	$-39.4°$	148.8	$2°$	$-35°$	$38°$	{easily fusible}
B.pt.	$-39.8°$	-52.3	$107°$	$125°$	$>175°$ (decomp.)	...

The heavier compounds dissociate on heating like the pentahalides. At $150°$ the vapour density of $POCl_3$ is still normal, at $275°$ it is too low. There are also oxy-compounds with mixed halogens, such as $POCl_2Br$ and $POBr_2Cl$. Fluorination of polymerised phosphonitrile chlorides, e.g. $(PNCl_2)_3$, has also been reported.[2]

The behaviour of these substances towards water is similar to that of the pentahalides, but the decomposition proceeds more slowly, since the oxyhalides are already the first hydrolytic products of the pentahalides. The compounds always fume in moist air, the fluorides most strongly. It is of interest that gaseous PSF_3 is spontaneously inflammable; as soon as it comes in contact with air it burns with a greenish-yellow flame.

It might be expected that it would be possible to replace two halogen atoms in the trihalides by O or S. These compounds may exist in the arsenic and phosphorus series—e.g. POCl or PSCl—but the descriptions found in the literature on the subject are doubtful. On the other hand, the bismuth and antimony compounds are well known and the oxygen compounds are none other than the basic "salts" precipitated by the action of water on the halogen compounds. In the bismuth salts hydrolysis of the halides leads to the exchange of two halogen atoms for one of oxygen very readily:

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl \qquad BiI_3 + H_2O \rightleftharpoons BiOI + 2HI.$$
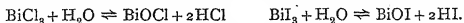
These oxyhalogen compounds are very sparingly soluble and separate as powders; the chloride and bromide are white, the iodide brick red; it may be used in the quantitative determination of bismuth, since it

[1] See Booth, et al., J. Amer. Chem. Soc., 1939, 61, 2927; 2934; 2937; 3120.
[2] Schmitz-Dumont and Kulkens, Z. anorg. Chem., 1938, 238, 189; 1938, 243, 143.

is precipitated from a dilute, weakly (nitric) acid solution of a bismuth salt on the addition of potassium iodide solution. The oxy-compounds of antimony are sparingly soluble microcrystalline powders which are more varied in type than the oxyhalides of bismuth. According to an investigation on the lines of the phase theory by van· Bemmelen, Meerburg and Noodt,[1] the three compounds $SbCl_3.SbOCl$, $SbOCl$ and $Sb_4O_5Cl_2$ exist as definite products of hydrolysis, but the last loses still more chlorine on treatment with excess of water. $Sb_4O_5Cl_2$ was formerly used in medicine as powder of Algaroth. It dissolves in hydrochloric acid and in tartaric acid, in which it forms complexes. Other antimony halides yield similar compounds.

The sulphohalides are also very well defined and crystalline :

SbSCl	SbSI	BiSCl	BiSBr	BiSI
Reddish brown.	Dark reddish brown.	Grey with metallic lustre.		

They are obtained by the action of sulphur, sulphuretted hydrogen or metallic sulphides on the halides, and are very stable to water.

Analogous selenium compounds are also known, such as BiSeCl.

Addition Products.—A very large series of ammines is formed by the tri- and even more by the penta-halides, *e.g.* :

$$PCl_3, 5NH_3 \qquad PCl_5, 8NH_3 \qquad PBr_5, 9NH_3 \quad . \quad BiCl_3.3NH_3$$
$$AsF_3, 3NH_3 \qquad AsCl_3, 4NH_3 \qquad SbCl_5, 6 \text{ and more } NH_3.$$

Their existence is somewhat surprising, since the halides are so extraordinarily susceptible to the action of water that ammonolysis might be expected. This actually takes place in the phosphorus compounds if the temperature is not kept sufficiently low. PCl_3 reacts at room temperature with gaseous ammonia with the elimination of HCl ; the compound $PCl_5.8NH_3$, however, only undergoes ammonolysis at about 175° with formation of phosphorus chloronitride, as described on p. 649. The compounds $SbCl_5.6NH_3$ and $BiCl_3.3NH_3$, however, can even be sublimed unchanged. BiI_3 can unite[2] with as many as 22 molecules of NH_3.

The addition compounds with the oxides of nitrogen and related substances are also very characteristic of this group ; they are mostly yellow and crystalline :

$$PCl_5, N_2O_4 \qquad BiCl_3, NO \qquad BiCl_3, NO_2 \qquad BiCl_3, NOCl$$
$$2SbCl_5, NO \qquad 3SbCl_5, 2NO_2 \qquad SbCl_5, NOCl \qquad 2SbCl_5, 5NOCl.$$

Only the compound $PCl_5N_2O_4$, which partially dissociates at room temperature, is white. The yellow sulphur compounds $SbCl_5S'$ and $SbCl_5, S_4N_4$ also belong to this class.

The number of double compounds with substances containing

[1] *Z. anorg. Chem.*, 1903, **33**, 272.
[2] Schwarz and Striebich, *Z. anorg. Chem.*, 1935, **223**, 399.

halogen is especially large. The following may be cited as examples of compounds with halides of non-metals:

$POCl_3$, BCl_3	PBr_3, BBr_3	PBr_5, BBr_3
PCl_5, ICl	$2PCl_5$, $SeCl_4$	AsF_3, SCl_4
$SbCl_5$, SCl_4	$SbCl_5$, SCl_4	$SbCl_5$, $SeOCl_2$
$SbCl_5$, PCl_5	$SbCl_5$, $POCl_3$	$SbCl_5$, SbF_5
$SbCl_5$, 2 or $3SbF_3$	$3SbCl_5$, $2SbF_5$	SbF_5, $3SbCl_5$.
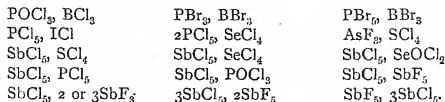
Again, one molecule of the following metal halides combines with one of the phosphorus halides, viz.:

$POCl_3$ and $MgCl_2$, $AlCl_3$, $SnCl_4$.

PBr_3 and $AuBr$, $PtBr_2$.

PCl_5 and $AuCl_3$, $MoCl_4$, $WoCl_6$, $TiCl_4$, $PtCl_4$, $SnCl_4$, UCl_5, $AlCl_3$, $CrCl_3$, $FeCl_3$, etc.
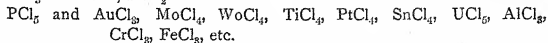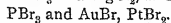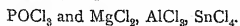
Werner regarded these compounds as chloro-salts; PCl_5 is the more negative, and the other the more positive, chloride. Against this view there is the fact that the strongly negative phosphorus in its halogen compounds forms very few double compounds (chlorosalts) with the halides of strongly positive metals, while antimony, which is much less negative, and even bismuth, are capable of doing so to a much greater extent. This may be due to the greater decomposition of the free phosphorus halides in water, so that they cannot exist in solution even in a large excess of halogen hydride. The behaviour of the trihalogen compounds of phosphorus with the noble metal halides is very interesting:

$PtCl_2$, $2PCl_3$ $PdCl_2$, PCl_3 $IrCl_3$, $3PCl_3$ $IrBr_4$, $2PBr_3$ $AuBr$, PCl_3

are formed. They may be considered as

$$\begin{bmatrix} Cl \diagdown \quad \diagup PCl_3 \\ \qquad Pt \\ Cl \diagup \quad \diagdown PCl_3 \end{bmatrix} \qquad \begin{bmatrix} Cl \diagdown \quad \diagup PCl_3 \\ Cl \!-\! Ir \!\Leftarrow\! PCl_3 \\ Cl \diagup \quad \diagdown PCl_3 \end{bmatrix}$$

etc., since the halogen co-ordinated with the metal is not replaceable by OH on hydrolysis, whereas that with the phosphorus may be exchanged, without the union between phosphorus and the metal being affected, thus giving

$$\begin{array}{c} Cl \diagdown \quad \diagup PCl_3 \\ \qquad Pt \\ Cl \diagup \quad \diagdown PCl_3 \end{array} \xrightarrow{+6H_2O} \begin{array}{c} Cl \diagdown \quad \diagup P(OH)_3 \\ \qquad Pt \\ Cl \diagup \quad \diagdown P(OH)_3. \end{array}$$
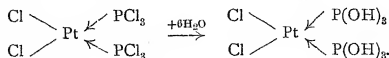
In this way a hexabasic acid is formed. Compounds of PCl_5 do not behave in this way; *e.g.* on dissolving platinum sponge in PCl_5 the ochre brown $PtCl_4$, $2PCl_5$ formed is completely decomposed by water with the formation of H_2PtCl_6.

The compounds which the halides of this group yield with the halogen salts of very positive metals may, however, be regarded as salts

of halogeno-acids. Only a few phosphorus compounds of this class are known; they are prepared in the dry way, e.g. those containing PCl_5 and the chlorides of bivalent metals. Their preparation is made difficult by the considerable decomposition which the phosphorus chloride undergoes in water. Alkali compounds of arsenic are also known of the type $3M^IX$, $2AsX_3$, as well as some double compounds of AsF_5.

The number of antimony and bismuth compounds belonging to these types is very large. Their stability is considerable, so that the hydrolysis of antimony and bismuth halides in the presence of metallic halides is greatly impeded; they dissolve in solutions of metal halides without separation of the basic salt. Sulphuretted hydrogen does not precipitate the antimony from the double fluorides of quinquevalent antimony, and in salts of the acid $H[SbCl_6]$ it can be shown that only two ions are formed in aqueous solution; the chlorine is so firmly attached to the antimony that silver nitrate only gives a precipitate slowly. Ammines of these salts may even be obtained in aqueous solution, but $SbCl_5$ is immediately decomposed by aqueous ammonia. The free halogen acid can sometimes be isolated; e.g. $HSbCl_6$, $4\frac{1}{2}H_2O$, which forms chlorine-coloured hygroscopic prisms which are stable in dry air, and $HSbBr_6$, which crystallises with three mols. water in black hygroscopic plates; H_3BiF_6, H_2BiBr_5 . $4H_2O$, $HBiI_4$ $4H_2O$ also exist.

Some other addition products of hydrogen halides and these halides are obtained, e.g. $2SbCl_3$, HCl, $2H_2O$ and $2BiCl_3$, HCl, $3H_2O$.

Like the free acids, the salts also have very many different formulae. Double compounds of the halides of tervalent antimony with metal halides are known (mainly only those of the alkalis, alkaline earths and of aluminium), in which the ratio of metal halide to Sb(Bi) halide has the following large range:

$$1:2 \quad 1:1 \quad 3:2 \quad 5:2 \quad 2:1 \quad 7:3 \quad 3:1 \quad 4:1.$$

Compounds such as those of the type $7:3$ or $4:1$ can only be explained with difficulty by the co-ordination theory, and the antimony compounds, $1:2$, e.g. $RbCl$. $2SbCl_3$. H_2O, are perhaps similar to HCl . $2BiCl_3$. $3H_2O$. The separate tervalent halide molecules may function differently in the complex. The colour of these salts, even when they are very complex, is influenced by that of the tervalent halide. Thus the compounds containing SbI_3 are red or black, those of $BiBr_3$ pale yellow, those of BiI_3 red to dark brown.

The double halides of quinquevalent antimony are very numerous. They are derived from the halogeno-acids, which correspond to the ortho-, pyro- and meta-acids containing oxygen:

Ortho: H_3SbO_4 Pyro: $H_4Sb_2O_7$ Meta: $HSbO_3$

H_3SbCl_8 H_2SbF_7; H_2SbCl_7 $HSbF_6$; $HSbCl_6$; $HSbBr_6$.
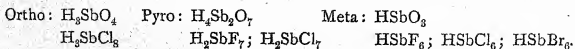
The number of chlorides is particularly large; they crystallise very well, and are not hygroscopic. The bromides, distinguished by their almost black colour, slowly lose bromine in air.

The halogen double salts of quadrivalent antimony, $M_2[SbX_6]$, are also nearly black (*cf.* pp. 331, 748), and are obtained from mixtures of the ter- and quinque-valent salts. These are very unstable in solution and easily separate into the ter- and quinque-valent portions. Only their compounds with the most voluminous bases are known.

Further, salts of mixed halogeno-acids may be obtained; *e.g.* from MCl and SbF_3, compounds $M[SbF_3Cl]$, or from $3MCl$ and $SbBr_3$ the compounds $M_3[SbCl_3Br_3]$. It is interesting that the same compounds are formed from $3MBr + SbCl_3$ as from $3MCl + SbBr_3$, so that after combination all halogens play similar parts.

The antimony compounds can also combine with salts other than those of halogen acids; *e.g.* double sulphates of the type M_2SO_4, SbF_3 and $M_2SO_4.2SbF_3$ are known, and oxalates of similar composition can be obtained, which are really very complex and from which the antimony cannot readily be precipitated.

Hydrofluophosphoric Acid and the Fluorinated Phosphoric Acids

$$HPF_6 \qquad OP{\overset{\textstyle OH}{\underset{\textstyle F_2}{<}}} \qquad OP{\overset{\textstyle (OH)_2}{\underset{\textstyle F}{<}}}$$

Hydrofluophosphoric acid.   Difluophosphoric acid.   Monofluophosphoric acid.

Whereas the halogen derivatives discussed above are all fairly rapidly or even instantaneously hydrolysed by water, the fluorine substitution products[1] of meta- and ortho-phosphoric acids are stable to water in much the same way as the fluorosulphonic acids (p. 596). The salts of HPF_6 can be boiled for a long time in strong alkali without decomposition, while their analogues, the salts of HBF_4 and H_2SiF_6, are readily decomposed in this way. The hydrofluophosphates, however, are hydrolysed by strong acids. The salts of the other two acids are stable in neutral solution, but less so in alkaline or acid solutions. The free acids are not so stable, though $OP(OH)_2F$ is not attacked by dilute alkalis.

All three acids are best made by heating phosphorus pentoxide with ammonium fluoride to about $135°$ or by adding the pentoxide to 40 per cent. hydrofluoric acid. NH_4PF_6 and KPF_6 can be made by the action of PCl_5 on the metallic fluoride. HPF_6 and $OP(OH)F_2$ may be isolated by means of the insoluble salts they form with nitron; the second of these acids gives well-crystallised compounds with alkaloids and with the alkali metals, particularly with caesium, though its other

[1] W. Lange, *Ber.*, 1928, 61, 799; 1929, 62, 782, 1054.

salts are hygroscopic. The heavy metal salts of HPF_6 are also soluble. Actually the acid

$$\left[\begin{array}{c} \bar{O}^\delta \\ \| + \\ \bar{O}^\delta = P = F^\delta \\ \| \\ F^\delta \end{array} \right] H \quad \text{resembles} \quad \left[\begin{array}{c} \bar{O}^\delta \\ ++\| + \\ \bar{O}^\delta = Cl = \bar{O}^\delta \\ \| \\ \bar{O}^\delta \end{array} \right] H$$
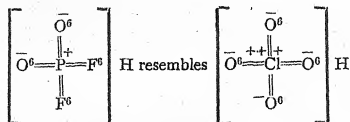
as the radii and co-ordination numbers of the ions are about the same. In the same way the monofluophosphoric acid

$$\left[\begin{array}{c} \bar{O}^\delta \\ \| + \\ \bar{O}^\delta = P = F^\delta \\ \| \\ \bar{O}^\delta \end{array} \right] H_2 \quad \text{resembles} \quad \left[\begin{array}{c} \cdot\bar{O}^\delta \\ +\| + \\ \bar{O}^\delta = S = \bar{O}^\delta \\ \| \\ \bar{O}^\delta \end{array} \right] H_2$$
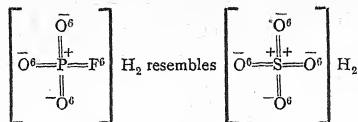
and the insoluble salts with the alkaline earths, lead and benzidine have about the same solubility products for the two acids.

The salts of the two monobasic acids are neutral to methyl orange and to phenolphthalein. Secondary alkali monofluophosphates are neutral to phenolphthalein; the primary salts are neutral to methyl orange.

VI. THE ELEMENTS OF THE FOURTH GROUP (AND BORON)

THE differences between the chemistry of carbon and that of the other elements considered in this section are very marked, in spite of the similarity in formula of many of their compounds. The chemistry of carbon owes its variety mainly to the symmetrical building power of the carbon atom, as compared with the heterogeneity of the substances which can be attached to it.[1] Hydrogen, oxygen, sulphur, nitrogen, halogens and even other carbon atoms can all be joined to carbon with approximately equal stability. In this peculiarity carbon is distinguished from all other elements, which have a definitely negative or positive bias.

Quadrivalent silicon shows quite different properties; its tendency to combine with negative radicals is much greater than with hydrogen. It is greater, for instance, with organic radicals and nitrogen, and reaches its maximum value with strongly negative elements like chlorine, fluorine and oxygen. In consequence, the bonds between silicon and other non-metals or other silicon atoms are readily ruptured by water in the cold, and replaced by the linkage Si—O.

The tendency of its oxygen compounds to polymerise spontaneously is a special characteristic of silicon; SiO_2 is not known in the unimolecular state like carbon dioxide. The importance of carbon in nature is largely due to the existence of the stable dioxide. After it has undergone countless chemical changes in plants and in animals it always reappears, transient but always present and ready to react anew, to give an abundance of organic compounds. With silicon, on the other hand, the pronounced tendency towards complex linkages with oxygen leads to petrifaction.

Boron and carbon have the smallest atomic volumes of all the elements; this has a definite influence on their capacity for forming chemical compounds. Although, other things being equal, elements of small volume tend to form complex compounds, this capacity is limited in those in which a very small volume accompanies a high primary valency. Sidgwick[2] has pointed out that the maximum covalency or co-ordination number of an element depends upon its

[1] Stock, *Ber.*, 1917, 50, 170.
[2] See *Ann. Rep. Chem. Soc.*, 1933, 30, 110.

position in the Periodic Classification; the maximum value is 2 for hydrogen, 4 for elements from Li to F, 6 for those from Na to Cl and from K to Br, and 8 for the remaining elements (see pp. 283 and 382). The behaviour of the halides towards water fits in with these values. It may be assumed that reaction takes place by formation of an additive compound, possibly produced only momentarily, in which the co-ordination number of the central atom is increased to its maximum by union with water. Thus in CCl_4 the carbon, having attained its maximum co-ordination number, cannot take up water and so is stable; but $SiCl_4$, containing silicon with maximum co-ordination number 6, can unite with water, $e.g.$ $SiCl_4(\leftarrow OH_2)_2$, and this union is followed by hydrolysis. Similarly, SeF_6 (maximum co-ordination number, 6) is not hydrolysed, but TeF_6 (maximum co-ordination number, 8) is decomposed by water.

A consideration of atomic dimensions[1] is important in connection with these problems, but it is doubtful if size is the determining factor in fixing covalency maxima. It has been argued, for example, that $[CF_6]''$ does not exist because there is insufficient space in which to pack six fluorine atoms around the smaller carbon atom, but $[SiF_6]''$ for the larger silicon atom represents a possible packing. In addition to the radii of the atoms, the nature of the chemical bonds is also important. Such bonds may be either of the ionic or of the covalent type, and although on general grounds it is highly improbable that in such compounds of carbon the bonds are of the ionic type, none the less the stereochemical possibilities of both types will be examined. The following are values for radii of atoms and ions; the radius of a positive ion, which has lost one or more electrons, is less than that of the neutral atom, and similarly the radius of a negative ion is greater than that of the neutral atom.

Radii of Atoms and Ions ($\mathring{A}.U.$).

C	0.77	C^{4+}	0.2	F	0.68	F^-	1.33
Si	1.17	Si^{4+}	0.4	Cl	0.97	Cl^-	1.81
S	1.06	S^{6+}	0.32	Br	1.13	Br^-	1.96
				I	1.35	I^-	2.19

The radii of quadrivalent positively charged C and Si cannot be measured direct, but are computed. Geometrically, it may be considered that the arrangement AB_4 is generally tetrahedral and in a few cases (see p. 348) planar; the valency angles will then be 109.5° and 90° respectively. For AB_6 the arrangement is octahedral, with valency angles of 90°, and for AB_8 cubic. Assuming that the atoms are spherical, that the radius of A is a and of B is

[1] For a discussion of the relation between atomic dimensions and valency, see L. Pauling, *Nature of the Chemical Bond*, 2nd Ed., Cornell University Press, 1940.
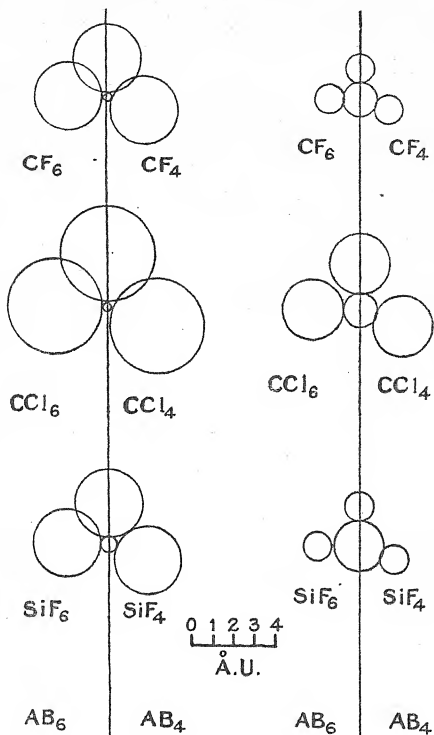
Fig. 59.

b, and that the limiting stage for stable molecules is that at which the spheres touch, then the maximum possible values of b are:

AB_4, tetrahedral	.	.	.	.	$b = 4 \cdot 45a$
AB_4, planar					
AB_6, octahedral	.	.	.	.	$b = 2 \cdot 42a$
AB_8 cubic	.	.	.	.	$b = 1 \cdot 37a$

The results are shown graphically for CF_4, CF_6, CCl_4, CCl_6, SiF_4 and SiF_6 (Fig. 59). The three diagrams on the left show the results for ionic

radii, and valency angles of 90° and 109·5° are considered. They show an overlap of spheres (except SiF_4 tetrahedral), illustrating the spatial impossibility of the existence of such compounds. On these grounds, as well as on others already accepted, the ionic formulation is debarred for these compounds of carbon and silicon.

When, however, the covalent union is considered, as in the diagrams on the right, the position is entirely different. Not only should CF_4 be stable, but there is ample room to pack six fluorine atoms about carbon; CI_6 also should be quite stable. It is apparent, therefore, that the ionic volumes are not the sole factors conditioning the formation of stable molecules. The unlinked atoms, each joined to a central atom cannot approach each other so closely that they make contact; it must be assumed that there is an external field, produced by the mutual repulsion of the outer electron shells which prevents geometrical contact. It is as if an envelope at least 0·5 Å.U. in thickness surrounds each atom, and in such discussions, the "field" effect is as significant as the radii of the atoms.

HYDRIDES AND HALIDES OF THE ELEMENTS OF THE FOURTH GROUP: OXIDES OF CARBON

Hydrides—Halides—Hydrofluosilicic and hydrofluoboric acids—Carbon monoxide —Carbonyls—Carbon dioxide—Carbonates—Thiocarbonates

The Hydrides

IN their tendency to give hydrogen ions, and thus to act as acids, the hydrides of this group form a continuation of the series HF $\longrightarrow$ H_2S $\longrightarrow$ NH_3 (p. 869). This property, already diminished in NH_3, is even smaller here. Therefore CH_4, SiH_4 and boron hydride are "neutral" hydrides. There are, however, compounds which may be represented by formulae in which the hydrogen in the above compounds has been replaced by metals. These are the carbides, borides, silicides and borohydrides, which do not, however, always correspond in formula to the hydrogen compounds of carbon, boron and silicon; additive compounds of boron hydrides and alkali metals have also been described.

Gaseous hydrogen compounds of germanium, tin and lead are likewise known, and from their properties seem to fit in with the above compounds.

Preparation.—The hydrogen compounds of this group are formed synthetically from the elements, or by reduction of other compounds with hydrogen, or by the hydrolysis of the metallic compounds. Hydrocarbons are prepared also by many other methods, described in text-books of organic chemistry.

Only in the synthetic preparation of the hydrogen compounds of carbon is a good yield obtainable. Pure carbon, either graphite or diamond, does not react appreciably with hydrogen, but at high temperatures it combines with hydrogen in the presence of a catalyst, particularly finely divided nickel or cobalt. These metals first form carbides and then these compounds react with hydrogen. In this way methane and acetylene are formed; at very high temperatures and under pressure higher saturated hydrocarbons are also obtained. A condition of equilibrium is set up, as the methane decomposes again into hydrogen and carbon. The higher the temperature the more the equilibrium lies on the side of the decomposition products. No

change occurs in a mixture of methane and hydrogen containing the following quantities:

At			300°	500°	600°	800°
CH_4	.	.	96·9	62·5	31·7	4·4 %
H_2	.	.	3·1	37·5	68·3	95·6 %

By the use of mixed catalysts hydrocarbons of both low and high carbon content can be obtained. The important method of Fischer and Tropsch leads to the formation of hydrocarbons up to solid paraffins by the action of mixed metal catalysts on water gas. Again, in the so-called "liquefaction of coal" in the Bergius process and its more recent modifications, the conversion of the carbon of coal into a mixture of hydrocarbons in the presence of catalysts is now a practicable process.[1]

The hydrogen compounds of the other elements of this group decompose at lower temperatures than methane; with these also direct synthesis, even when it is successful, gives only small yields at temperatures at which some appreciable reaction velocity may be expected. The decomposition of the hydrides to hydrogen and a mirror of the element affords a useful method for their analyses.

The reduction of other compounds to hydrogen compounds is best accomplished by nascent hydrogen, although carbon tetrachloride, CCl_4, or carbon disulphide, CS_2, also gives methane on heating with molecular hydrogen. For the hydrides of B, C and Si this mode of formation has only a systematic interest. On the other hand, germanium hydride may be prepared by treating germanium tetrachloride, $GeCl_4$, with zinc and acid, corresponding to the method used for the hydrides of arsenic and antimony,[2] or by reduction with overvoltage at a lead cathode.[3] The most convenient method for preparing all other hydrogen compounds is the hydrolysis of carbides, borides and silicides, or of the alloys of lead and tin with other metals.

$$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$$
$$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2,$$
$$Mg_2Si + 4H_2O \longrightarrow 2Mg(OH)_2 + SiH_4,$$
$$Mg_2Sn + 4H_2O \longrightarrow 2Mg(OH)_2 + SnH_4, \text{ etc.}$$
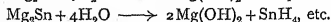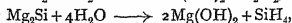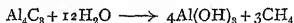
Whereas carbides of all metals give hydrocarbons with water or acids, magnesium silicide, boride, stannide, etc., are the only compounds extensively used for the preparation of the other hydrogen compounds of this group, as they are hydrolysed by dilute acid. For rough experiments silicon and boron hydrides may be obtained by mixing metallic magnesium with SiO_2 or B_2O_3 respectively, and heating the mixture at one spot; the reaction once begun proceeds of its own accord, and the resulting silicon or boron unites with the excess of

[1] Cf. C. H. Lander, *Nature*, 1932, 129, 640.
[2] Voegelin, *Z. anorg. Chem.*, 1902, 30, 325.
[3] Paneth and Rabinowitsch, *Ber.*, 1925, 58, 1138.

magnesium to form a silicide or boride. These yield the hydrogen compounds of silicon or boron when hydrochloric or sulphuric acid is added. The quantities obtained are small (4-5 per cent.), since the hydrogen compounds, especially the boron compound, immediately react with water; the yields are improved (11 per cent.) by using 8N-phosphoric acid[1] at 40-50°. B_2H_6, which had been prepared with difficulty by heating B_4H_{10} at 100°, has been made in quantity by Schlesinger and Burg[2] by utilising the reversible reaction $6B_2H_5Cl \rightleftharpoons 5B_2H_6 + 2BCl_3$; a mixture of BCl_3 and H_2 under the influence of a silent electric discharge forms B_2H_5Cl, which then gives B_2H_6 as shown. Instead of BCl_3, BBr_3 may be used with advantage. Greatly improved yields of silanes[3] or of germanium hydrides[4] are obtained by adding magnesium silicide or germanide to ammonium bromide in liquid ammonia.

Borides other than that of magnesium give very little boron hydride or none at all, though beryllium boride behaves like Mg_3B_2 and the gas obtained from it has the advantage of being free from silanes.

Composition.—The composition of the hydrocarbon formed depends upon that of the carbide employed. The carbides of the alkali and alkaline earth metals give only acetylene, C_2H_2; they are all composed in such a way that the hydrogen of the acetylene is replaced by an equivalent number of metal atoms, *e.g.* Li_2C_2, K_2C_2, CaC_2, etc. The formation of acetylene can thus be represented as a hydrolysis:

$$Li_2C_2 + H_2O \longrightarrow Li_2O + C_2H_2 \qquad CaC_2 + H_2O \longrightarrow CaO + C_2H_2.$$

In the same way the carbides of aluminium and beryllium give only methane:

$$Al_4C_3 + 6H_2O \longrightarrow 2Al_2O_3 + 3CH_4 \qquad Be_2C + 2H_2O \longrightarrow 2BeO + CH_4.$$
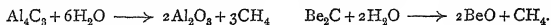
Other carbides cannot be represented as hydrocarbons substituted by metals, and if the metal in them were replaced by hydrogen no known hydrocarbon would be obtained. To these belongs, for example, manganese carbide, Mn_3C; it does not give a hydrocarbon, CH_6, but evolves a mixture of CH_4 and H_2 instead. The carbides of the rare earths, such as thorium, uranium, etc., to which the formulae CeC_2, ThC_2, U_2C_3 are given, act in a still more complicated manner, and give a mixture of most varied hydrocarbons, gaseous, liquid and solid.

Magnesium silicide, germanide and boride, which have the formulae Mg_2Si, Mg_2Ge and Mg_3B_2, behave similarly to these carbides, and instead of giving SiH_4, GeH_4 and BH_3 on hydrolysis, a mixture of

[1] Steele and Mills, *J. Amer. Chem. Soc.*, 1930, 52, 74.
[2] *J. Amer. Chem. Soc.*, 1931, 53, 4321.
[3] Johnson and Hogness, *J. Amer. Chem. Soc.*, 1934, 56, 1252.
[4] Kraus and Carney, *ibid.*, 765.

very varied hydrogen compounds is obtained, which has been the subject of extensive work by Stock and his pupils.[1] Magnesium silicide always contains oxygen, which may be present in the form of "hyposilicates" (compare hypoborates, p. 840). It is specially worthy of notice that BH_3 is not produced, but instead, in addition to other boron hydrides, the main product is B_4H_{10}, tetraborane. BH_3 is not known, the simplest compound being diborane, B_2H_6 and BH_3CO (p. 779) is also known. Burg and Schlesinger[2] consider that evidence for BH_3 is obtained in the decomposition of $BH_3.CO$. It may be mentioned that boron trimethyl, $B(CH_3)_3$, and boron triethyl, $B(C_2H_5)_3$, show no tendency to polymerise, but boron triethyl decomposes on heating, yielding hydrogen and ethane.

BH_4 is probably not known, but one of its derivatives, hypoboric acid, $H_2B.OH$, is known in the form of its salts.

Diborane, B_2H_6, is a compound in which boron is joined to boron, just as in ethane carbon is linked to carbon. This is apparent from the successive replacement of hydrogen by halogen, when, for example, $H_2B.BH_2Br$ is formed, which can scarcely be interpreted as an additive compound BH_3, BH_2Br. On complete bromination BBr_3 is obtained. With halogens in place of hydrogen, BX_3 gives octets of electrons, the three boron electrons being shared, and thus completing the octets of the halogen atoms, but boron has a shell of six electrons.

In the decomposition of magnesium silicide, Mg_2Si, by acids, a number of silicon hydrides are formed simultaneously, in decreasing amounts, from SiH_4 to Si_6H_{14}. The volatile silicon hydrides correspond in their formulae to the hydrocarbons of the methane series; up till now none with more than six silicon atoms has been definitely recognised. On the other hand, the whole series of the hydrides of boron may not be known, but some liquids, B_5H_9 and B_6H_{10}, some solids, of which B_8H_{14} has been adequately studied, and three more, probably B_5H_4 B_6H_{12}, and one with twelve boron atoms, which are obtained by the decomposition of the lower members, are known. The well-established boron hydrides are all of two general types, boranes, B_nH_{n+4}, and dihydroboranes, B_nH_{n+6}, the former being the more stable.

Germanium, tin and lead hydrides may be detected by a reaction analogous to the Marsh test for arsenic. In the germanium series GeH_4, Ge_2H_6 and Ge_3H_8 are known[3] and also the solid hydrides[4] $(GeH)_x$ (brown) and $(GeH_2)_x$ (yellow), prepared respectively by the reaction of NaGe with water and of CaGe with acid. The tin hydride,

[1] Boron hydrides, *Ber.*, 1912-14, **45-47**; silicon hydrides, *Ber.*, 1916-20, **49-52**, and collected in *Ber.*, 1921, **54**, 142; see also "Hydrides of Boron and Silicon," Stock, Cornell University Press, 1933.

[2] *J. Amer. Chem. Soc.*, 1937, **59**, 780.

[3] Dennis, Corey and Moore, *J. Amer. Chem. Soc.*, 1924, **46**, 657.

[4] Dennis and Skow, *J. Amer. Chem. Soc.*, 1930, **52**, 2369; Royen and Schwarz, *Z. anorg. Chem*, 1933, **211**, 412; **215**, 295.

SnH_4, and the lead hydride, PbH_4, are the only types known in those series.

The silicon hydrides are described as silanes (SiH_4, monosilane, Si_2H_6, disilane, then tri, tetra, etc., -silanes); the boron hydrides, B_2H_6 and B_4H_{10}, are called diborane and tetraborane. The separation of those directly formed from the magnesium alloys and acid, *i.e.* B_4H_{10}, B_5H_9, B_6H_{10} and $B_{10}H_{14}$ and the mixed silanes, is carried out by liquefaction of the gases and fractional distillation; B_2H_6, B_5H_9, and B_6H_{12}(?) are obtained by heating tetraborane. B_2H_6 can be isolated pure most easily, but the purification of B_4H_{10} is difficult. The molecular weight of all these compounds is found to be in agreement with the above formulae.

Properties.—The following table gives the melting and boiling points of these hydrides; the properties of the corresponding paraffins are also given. The structures of B_2H_6 and C_2H_6 as determined by the X-ray method are similar, while that of Si_2H_6 is different. The ultra-violet absorption spectrum of B_2H_6 is much more like that of C_2H_4 than that of C_2H_6, and that of B_4H_{10} resembles that of butadiene, $CH_2:CH.CH:CH_2$. The melting and boiling points of boron and carbon hydrides lie fairly close together and the analogy is continued in the substitution products, B_2H_5Br and C_2H_5Br, B_2H_5I and C_2H_5I.

	CH_4	SiH_4	GeH_4	SnH_4	C_2H_6	Si_2H_6	Ge_2H_6	B_2H_6
Melting point	$-184°$	$-185°$	$-165°$	$-150°$	$-172.1°$	$-132.5°$	$-109°$	$-165.5°$
Boiling point	$-160°$	$-112°$	$-88°$	...	$-88.3°$	$-14.5°$	$+29°$	-92.5

	C_3H_8	Si_3H_8	Ge_3H_8	C_4H_{10}	Si_4H_{10}	B_4H_{10}
Melting point	$-190°$	$-117.4°$	$-105.6°$	$-135°$	$-93.5°$	$-120°$
Boiling point	$-45°$	$+53°$	$+110.5°$	$+0.6°$	$+109°$	$+18°$

B_5H_9, liquid, m.pt. $-47°$; vapour pressure at $0°$, 66 mm.
B_5H_{11}, liquid, m.pt. $-123°$; vapour pressure at $0°$, 53 mm.
B_6H_{10}, liquid, m.pt. $-65°$; vapour pressure at $0°$, 7 mm.
$B_{10}H_{14}$, needles, m.pt. $99.5°$; b.pt. $213°/1$ atm.
Si_5H_{12}, vapour pressure at $0°$, ca. 1.5 mm.
Si_6H_{14}, vapour pressure at $15°$, ca. 1 mm.

B_5H_4 and $B_{12}H_x$ are non-volatile solids, the former yellow and insoluble in carbon disulphide, and the latter colourless and soluble in carbon disulphide. $B_{26}H_{36}$ possibly results as a yellow solid, readily soluble in benzene, from the spontaneous decomposition of B_6H_{10} at room temperature. There is also a solid yellow silicon hydride of unknown composition.

The silanes and boranes are also, up to the tetra-compounds, gaseous and colourless at the ordinary temperature. Their similarity to the carbon compounds is limited to their formulae and physical state; their chemical properties are altogether different from those of the paraffins, for they are extremely reactive substances. Silanes react immediately with the oxygen of the air, usually with violent explosion; large gas-holders of SiH_4 explode on the admission of air. They impart

spontaneous inflammability to hydrogen when mixed with it. Pure boranes are not spontaneously inflammable in air.

Silicon and boron hydrides resemble antimony or arsenic hydride in many respects. Like these they decompose at a high temperature, the free elements being deposited in the form of mirrors. Similarly, they are very poisonous, and on being inhaled even in small quantities cause headache and sickness. In contrast to the hydrocarbons, they possess a stupefying, highly nauseating chocolate-like odour resembling, in low concentrations, antimony hydride, in larger quantities, sulphuretted hydrogen.

The lower silanes may be kept unchanged in sealed vessels at the ordinary temperature; diborane decomposes very slowly (six months) under these conditions, giving some $B_{10}H_{14}$, traces of H_2 and B_5H_{11} and a liquid hydride, which in turn splits up into H_2 and $B_{10}H_{14}$. Tetrasilane and tetraborane, however, undergo rather more rapid decomposition even at room temperature; Si_2H_6 first begins to decompose at about 300°, B_2H_6 at a much lower temperature. Just above 100° it is measurably rapidly decomposed, and hence the chief products from the tetraborane formed by the hydrolysis of magnesium boride are the other compounds of boron and hydrogen, which can be separated by fractional distillation. Ultra-violet light brings about a similar decomposition; at red heat a more complete decomposition into hydrogen and silicon or boron respectively takes place. Pure tin hydride is also stable for some days in clean smooth glass vessels, but decomposes more rapidly if the container is rough or "infected." It breaks up immediately at 150°.

On account of their neutral reaction boron and silicon hydrides are inert to many reagents, e.g. concentrated sulphuric acid. Tin hydride is unaffected by dilute alkalis, dilute sulphuric acid, most metallic salt solutions, and even by concentrated nitric acid. Like SbH_3, however, it is absorbed by solutions of $AgNO_3$ or $HgCl_2$, and also by solid alkalis and concentrated sulphuric acid. It gives characteristic colours to the hydrogen flame: first a reddish colour, then as the concentration is increased a luminous yellow with a blue mantle. In this way concentrations of 0·002 per cent. upwards may be detected. The tin mirror is light grey in colour and develops a silvery sheen when deposition is prolonged.[1]

Boranes and silanes are readily decomposed by oxidising agents. They dissolve without decomposition in many organic solvents, but it is interesting to notice that Si_2H_6 and Si_3H_8 react with chloroform or carbon tetrachloride with the most violent explosion. The hydrogen atoms may be replaced step by step by halogen, but in the boranes all the stages of the substitution are not yet known. B_2H_6 reacts explosively with Cl_2 at room temperature; with Br_2, the reaction is

[1] F. Paneth and E. Rabinowitsch, Ber., 1924, 57, 1877.

fairly rapid at 100° and B_2H_5Br and BBr_3 can be isolated. B_2H_5Br changes completely in a week to B_2H_6 and BBr_3 (compare preparation of B_2H_6 from B_2H_5Cl, p. 765). $B_{10}H_{14}$, one of the most stable of the boron hydrides, yields $B_{10}H_{12}Br_2$ and $B_{10}H_{11}Br_3$ after long-standing with bromine, so that $B_{10}H_{14}$ cannot be regarded as an unsaturated compound. The behaviour of silanes and boranes towards the halogen acids is notable. With these a double decomposition takes place in the presence of aluminium chloride or bromide: $SiH_4 + HCl \longrightarrow SiH_3Cl + H_2$, a reaction which the hydrocarbons do not give. B_2H_6 similarly gives B_2H_5Cl, and with hydriodic acid, B_2H_5I is obtained. The mobility of the hydrogen atoms in the silanes and boranes is also shown by their behaviour towards water; in the silanes the whole of the hydrogen atoms are removed:

$$SiH_4 + 2H_2O \longrightarrow SiO_2 + 4H_2; \; Si_2H_6 + 4H_2O \longrightarrow 2SiO_2 + 7H_2.$$
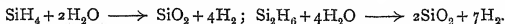
With caustic soda, in an analogous way, sodium silicate is formed instead of silicic acid. Hydrolysis by alkali is much more rapid than is that by water; e.g. some silanes can be kept in quartz vessels in presence of water, but in glass vessels they are unstable, owing to alkali dissolved from the glass. The rates of hydrolysis of the boranes by water differ widely; B_4H_{10} is hydrolysed slowly, 50 per cent. decomposition taking place at room temperature in two hours; B_2H_6 is hydrolysed almost instantaneously, and this no doubt accounts for its non-appearance during the decomposition of Mg_3B_2 by acid:

$$B_2H_6 + 6H_2O \longrightarrow 2B(OH)_3 + 6H_2; \; B_4H_{10} + 12H_2O \longrightarrow 4B(OH)_3 + 11H_2.$$
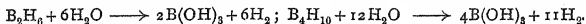
Here the decomposition occurs by way of an intermediate product, hypoboric acid, $H_3B \cdot OH$, which may be isolated if the decomposition is carried out by alkaline solutions. The elimination of hydrogen then proceeds slowly, and only ensues after the acid is formed. B_5H_9, B_6H_{10} and $B_{10}H_{14}$ are only slowly decomposed by water, their reactivity diminishing with increasing molecular weight.

Boron hydrides, B_nH_{n+4}, give a series of solid non-volatile addition products with ammonia, in which the ammonia is firmly attached; those formed from B_nH_{n+6}, if they exist, are unstable. The following have been obtained: $B_2H_6 \cdot 2NH_3$, $B_5H_9 \cdot 4NH_3$, $B_{10}H_{14} \cdot 6NH_3$ and $B_4H_{10} \cdot 4NH_3$. It is probable that $B_2H_6 \cdot 2NH_3$ is a monoammonium salt of the formula $NH_4^+H_3BNH_2BH_2^-$, i.e. containing a B—N—B chain (see p. 774). The most interesting reaction[1] of these addition compounds is that with HCl:

$$B_2H_6(NH_3)_2 + 2HCl \longrightarrow B_2H_4Cl_2(NH_3)_2 + 2H_2.$$
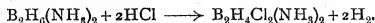
When heated in a sealed tube these ammines give $B_3N_3H_6$ (p. 637).

[1] Stock and Pohland, Ber., 1926, 59, 2210.

Many of the properties of these addition products suggest their similarity to ammonium compounds.

Borine carbonyl, BH_3CO (b.pt. $-64°$) is prepared by heating diborane and carbon monoxide together, when an equilibrium is set up:

$$B_2H_6 + 2CO \rightleftharpoons 2BH_3CO$$
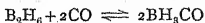
At 200 mm. pressure and 100°, the mixture contains 5% BH_3CO, which can be isolated by rapidly cooling the equilibrium mixture. It forms an addition compound with ammonia $BH_3CO(NH_3)_2$.

An interesting series of *metal borohydrides* has been prepared by the interaction of metal alkyls and diborane.[1] While the aluminium borohydride AlB_3H_{12} (m.pt. $-64.5°$, b.pt. $44.5°$) is soluble in benzene and probably non-polar, the lithium compound $LiBH_4$ (m.pt. 275° decomp.) is insoluble in benzene and probably polar. The beryllium borohydride BeB_2H_8 (m.pt. 123°, b.pt. 91.3°) is accompanied by the nonvolatile $BeBH_5$ and is intermediate in type. Similarly, while the lithium compound is stable in dry air, aluminium borohydride is spontaneously inflammable like diborane.

These borohydrides may be contrasted with the borane salts prepared by Stock[2] by the action of amalgam on the hydrides: $B_2H_6 + K_2 \longrightarrow K_2B_2H_6$. The product could be heated to 300° without change. These white solids decompose at higher temperatures with evolution of hydrogen.

Constitution of the Boron Hydrides.—It would appear that the constitution of the boron hydrides cannot be explained on the basis of electrovalency. The volatility of the hydrides further suggests their non-polar character. The simplest of them, B_2H_6, contradicts at the outset the idea of tervalent boron. Many theories have been put forward to explain the arrangement of electrons in these compounds, but a completely satisfactory solution of the problem does not appear to have been reached.[3] Among the ideas which have been brought forward are the following: a linkage between two atoms due to one electron only, the sharing of electrons between four atoms (Wiberg), or the utilisation of the inner electrons of the boron atom for the completion of the octets.

It has been suggested that octets in B_2H_6 are completed by utilising two electrons from the K level; this view must be rejected, however, on account of the energy changes involved.

The formation of ammonia addition products by the hydrides has been considered to show the presence of acidic hydrogen. The modern view of

[1] Schlesinger and co-workers, *J. Amer. Chem. Soc.*, 1939, 61, 536 : 1940, 62, 3421, 3425, 3429.

[2] *Z. anorg. Chem.*, 1935, 225, 225 ; 1936, 228, 178.

[3] For earlier literature, see E. Wiberg, *Z. anorg. Chem.*, 1928, 173, 199 ; Stock, "The Hydrides of Boron and Silicon," p. 213.

the structure of these ammines is discussed on p. 773. The following remarks, however, indicate the lines on which earlier ideas were based. Main Smith held the view that $B_2H_6 . 2NH_3$ is really $BH_3 . NH_3$ of electronic formula $H_3B \leftarrow NH_3$, analogous to $(CH_3)_3B \leftarrow NH_3$. But B_2H_6 in liquid ammonia is feebly conducting, a fact which has led to the suggestion

that $B_2H_6 . 2NH_3$ is $[B_2H_4](NH_4)_2$, i.e. $\left[\begin{array}{c} H \\ H \end{array} \!\!\! \diagup \!\! \overline{B} \!\! = \!\! \overline{B} \!\! \diagdown \!\!\! \begin{array}{c} H \\ H \end{array} \right] (NH_4)_2$ and the

hydride, therefore, is $\left[\begin{array}{c} H \\ H \end{array} \!\!\! \diagup \!\! \overline{B} \!\! = \!\! \overline{B} \!\! \diagdown \!\!\! \begin{array}{c} H \\ H \end{array} \right] (H^+)_2$. The hydrides B_2H_6 and

B_4H_{10} give with sodium the additive compounds $B_2H_6 . 2Na$ and $B_4H_{10} . 2Na$, which are formulated as:

$$\left[\begin{array}{c} H \\ H \!\!-\!\! \overline{B} \!\!-\!\! \overline{B} \!\!-\!\! H \\ H \end{array} \diagup\!\!\!\!\diagdown \begin{array}{c} H \\ \\ H \end{array} \right] (Na^+)_2 \text{ and } \left[\begin{array}{c} H \\ H \end{array} \!\!\!\diagup\!\! \overline{B} \!\!=\!\! \overline{B} \!\!-\!\! \overline{B} \!\!=\!\! \overline{B} \diagdown \!\!\!\begin{array}{c} H \\ H \end{array} \right] H_4Na_2$$
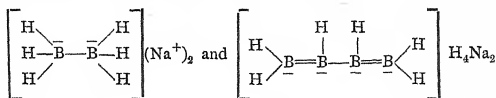
for the ammonia compound of the second is $B_4H_{10} . 4NH_3$. Although B_5H_9 forms a tetrammine, the hydride must be assumed pentabasic:

$$\left[\begin{array}{c} H \\ H \end{array} \!\!\!\diagup\!\! \overline{B} \!\!=\!\! \overline{B} \!\!=\!\! \overline{B} \!\!=\!\! \overline{B} \!\!=\!\! \overline{B} \diagdown \!\!\!\begin{array}{c} H \\ H \end{array} \right] H_5 \text{ if the octet-duplet rule is to be}$$
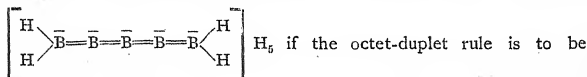
maintained. The other hydrides are shown similarly, and a bicyclic structure has been used for $B_{10}H_{14}$. These ammines react readily with hydrogen chloride and such changes are difficult to reconcile with these formulae, e.g.:

$$B_2H_4(NH_4)_2 + 2HCl \longrightarrow B_2H_2Cl_2(NH_4)_2 + 2H_2$$
$$B_4H_6(NH_4)_4 + 8HCl \longrightarrow B_4Cl_6(NH_4)_4 + 7H_2$$
$$2(B_5H_4)H(NH_4)_4 + 14HCl \longrightarrow 2(B_5Cl_7)H(NH_4)_4 + 11H_2.$$
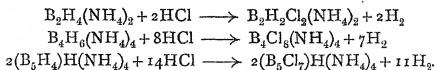
The volatility of the hydrides suggests that they are covalent, and not electrovalent types. Also they behave generally as saturated, and not unsaturated, compounds (see reactions with halogens, p. 769).

They have also been represented with single electron linkages, e.g.:

$$\begin{array}{ccc} H^{+\frac{1}{2}} & H^{+\frac{1}{2}} & \\ | & | & \\ H\!\!=\!\!B\!\!\equiv\!\!B\!\!=\!\!H & & H\!\!=\!\!B\!\!-\!\!B\!\!=\!\!H \\ | & | & \\ H^{+\frac{1}{2}} & H^{+\frac{1}{2}} & \end{array} \qquad \begin{array}{c} H\!\!-\!\!H \\ \\ H\!\!=\!\!B\!\!-\!\!B\!\!=\!\!H \\ \| \quad \| \\ H \quad H \end{array}$$

If the boron hydrides contain singlets, they should be paramagnetic and should, therefore, accelerate the conversion from para- to ortho-hydrogen. Farkas and Sachsse[1] found, however, no acceleration with B_2H_6.

B_2H_6 has 12 valency electrons, and theoretical considerations lead to the conclusion that the molecule is in a state of resonance between the seven Lewis structures such as

$$H \quad H \qquad\qquad H+ \ H$$
$$H:B \quad B:H \quad , \quad H:B \ : \ B^- : H \quad , \text{ etc.}$$
$$H \quad H \qquad\qquad H \quad H$$
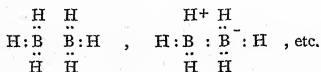
(in which each bond has six-sevenths single-bond and one-seventh no-bond character) and the one-electron bond structures such as

$$H \quad H$$
$$H \cdot B \ : \ B \cdot H \quad , \text{ etc.}$$
$$H \quad H$$
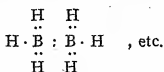
This view is substantiated by the measurement[2] of the B—B and B—H distances, which are much larger than the corresponding single covalent bond distances. The structures of B_5H_9, B_6H_{10} and $B_{10}H_{14}$ follow from this fundamental idea. They all consist of $B_2H_6 \cdot n BH$ where $n = 3$, 4 and 8.

B_5H_9 is believed to have the cyclic structure
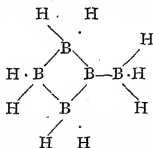
and B_6H_{10} and $B_{10}H_{14}$ are probably best represented by:
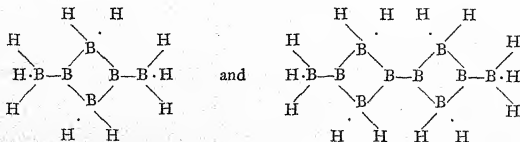
[1] *Trans. Faraday Soc.*, 1934, **30**, 331.
[2] S. H. Bauer, *J. Amer. Chem. Soc.*, 1937, **59**, 1096.

B_4H_{10} may be shown as:

$$
\begin{array}{c}
\text{H} \quad \text{H} \quad \text{H} \qquad \text{H} \\
\cdot \quad | \qquad \cdot \quad / \\
\text{B} \qquad \text{B} \qquad \text{H} \\
/ \quad \diagdown \qquad / \quad \diagdown \\
\text{H} \qquad \text{B} \qquad \text{B} \\
/ \quad \diagdown \quad / \quad \cdot \\
\text{H} \quad \text{H} \ \text{H} \quad \text{H}
\end{array}
$$

and B_5H_{11} similarly:
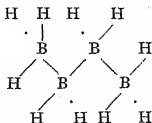
$$
\begin{array}{c}
\text{H} \quad \text{H} \qquad \text{H} \quad \text{H} \\
| \qquad \cdot \ / \qquad | \\
\text{H} \cdot \text{B} \qquad \text{B} \qquad \text{B} \cdot \text{H} \\
/ \quad \diagdown \quad \diagdown \quad / \quad \diagdown \\
\text{H} \qquad \text{B} \qquad \qquad \text{B} \qquad \text{H} \\
/ \quad \cdot \qquad / \quad \cdot \\
\text{H} \quad \text{H} \ \text{H} \qquad \text{H}
\end{array}
$$
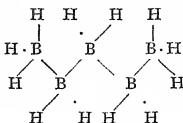
In all the above formulae it must be understood that the one- and two-electron bonds are in resonance, and that each bond is really equivalent to every other bond.

Wiberg's formula for B_2H_6, $[H_2=B=B=H_2]'' \ 2\overset{+}{H}$ is supported by parachor measurements (observed parachor, 121·9; calculated, 121·2). But in electron diffraction measurements, the B — B link is not shortened, so. that B=B is unlikely, and the B—H link is longer than normal, suggesting that this bond is weaker. These observations support the view of G. N. Lewis, indicated on p. 772, that B_2H_6 has an ethane structure except for a deficiency of 2 electrons and that the six pairs oscillate between seven possible positions. Thus each pair is only present for 6/7ths of the time with a consequent decrease in bond stability and a slight increase in the interatomic distance. In borine carbonyl the B—C—O group is linear, the H atoms completing the borine tetrahedron. $BH_3N(CH_3)_3$ has a similar structure. Resonance occurs between

$$
\begin{array}{cc}
\text{H} & \text{H} \\
\overset{-}{\text{H}:\overset{..}{\text{B}}}:\text{C}:::\overset{+}{\text{O}}: & \text{and} \quad \text{H}:\overset{..}{\overset{-}{\text{B}}}: \ \overset{+}{\text{C}}::\overset{..}{\text{O}}: \\
\overset{..}{\text{H}} & \overset{..}{\text{H}}
\end{array}
$$
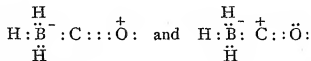
The structure of the boron hydride ammoniates has been deduced from accumulated miscellaneous data; the most conclusive evidence arises from the discovery of the compound B_2H_7N (b.pt. 76·2°, m.pt. −66·5°), which is formed when diborane diammoniate, $B_2H_6.2NH_3$, is prepared using excess of diborane. This substance forms an addition product with trimethylamine, Me_3N, B_2H_7N, and also an ammoniate, B_2H_7N, NH_3. The latter, on rapidly heating to 200°, forms $B_3N_3H_6$ (see p. 769). Since $B_3N_3H_6$ is almost certainly a cyclic compound
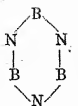
involving the ring $\begin{array}{c} B \\ N \quad N \\ | \quad | \\ B \quad B \\ N \end{array}$, it is natural to infer that the B—N—B chain occurs in B_2H_7N, which is given the structure:
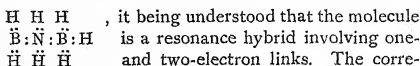
$$\begin{array}{ccc} H & H & H \\ \ddot{B}:\ddot{N}:\ddot{B}:H \\ H & H & H \end{array}$$, it being understood that the molecule is a resonance hybrid involving one- and two-electron links. The corresponding ammoniate may be indicated by

$$\begin{array}{cccc} H & H & H & H \\ | & | & | & | \\ H—B—N—B—N—H \\ | & | & | & | \\ H & H & H & H \end{array}$$
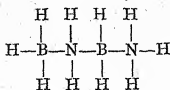
By analogy with this structure, and in view of the demonstrable monoammoniate nature of diborane diammoniate, we may write the latter:

$$NH_4^+[BH_3 . NH_2 . BH_3]^-.$$
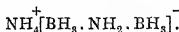
Halogen Compounds

The hydrogen in the hydrides of boron, carbon and silicon may be replaced by halogen, atom for atom. A series of compounds is thus produced, of which up till recently only those containing carbon were well known. The chlorine and bromine compounds are the commonest; their melting and boiling points are given in the following table (boiling points in *italic*):

$CH_4 \begin{smallmatrix} -184° \\ -160° \end{smallmatrix}$	$CH_3Cl \begin{smallmatrix} -91.5° \\ -24° \end{smallmatrix}$	$CH_2Cl_2 \begin{smallmatrix} -97° \\ +40° \end{smallmatrix}$	$CHCl_3 \begin{smallmatrix} -63° \\ +61° \end{smallmatrix}$	$CCl_4 \begin{smallmatrix} -23° \\ +77° \end{smallmatrix}$
$SiH_4 \begin{smallmatrix} -185° \\ -112° \end{smallmatrix}$	$SiH_3Cl \begin{smallmatrix} -118° \\ -30° \end{smallmatrix}$	$SiH_2Cl_2 \begin{smallmatrix} -122° \\ +8° \end{smallmatrix}$	$SiHCl_3 \begin{smallmatrix} -126.6° \\ +31.8° \end{smallmatrix}$	$SiCl_4 \begin{smallmatrix} -69° \\ +57° \end{smallmatrix}$
	$CH_3Br \begin{smallmatrix} -93° \\ 4.5° \end{smallmatrix}$	$CH_2Br_2 \quad \overline{98.5}$	$CHBr_3 \begin{smallmatrix} 7.8° \\ 146.5° \end{smallmatrix}$	$CBr_4 \begin{smallmatrix} 92.5° \\ 189.5° \end{smallmatrix}$
	$SiH_3Br \begin{smallmatrix} -94° \\ +2° \end{smallmatrix}$	$SiH_2Br_2 \begin{smallmatrix} -70.1° \\ +66° \end{smallmatrix}$	$SiHBr_3 \begin{smallmatrix} < -60° \\ +111° \end{smallmatrix}$	$SiBr_4 \begin{smallmatrix} +5° \\ 153° \end{smallmatrix}$

Of the partially substituted halogen derivatives of boron hydride the compound B_2H_5Br is adequately known [1] (m.pt. $-104°$, b.pt. $10°$). $B_{10}H_{14}$ also reacts with bromine with the substitution of hydrogen by bromine (see p. 769).

Partially Halogenated Products.—The silicon halogen hydrides are best formed by double decomposition between the gaseous halogen hydride and SiH_4 at $100°$-$200°$, a reaction which cannot be obtained with the corresponding carbon compounds:

$$SiH_4 + HCl \longrightarrow SiH_3Cl + H_2 \qquad SiH_4 + 2HBr \longrightarrow SiH_2Br_2 + 2H_2, \text{ etc.}$$
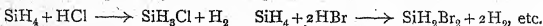
[1] Stock, Kuss and Priess, *Ber.*, 1914, 47, 3115.

These reactions take place only in the presence of active $AlCl_3$ or $AlBr_3$ as catalysts, of which even traces are sufficient to complete the reaction in a short time. SiH_4 or B_2H_6 can be treated with halogen direct: $SiH_4 + Br_2 \longrightarrow SiH_3Br + HBr$, but this procedure may easily be explosive and must therefore be made at very low temperatures and at great dilutions.[1] $SiHCl_3$ and $SiHBr_3$ (silico- chloroform and -bromoform) are most conveniently obtained by another method—by heating crystalline silicon, or better a metallic silicide (copper silicide), in a current of halogen hydride. Silico-iodoform, $SiHI_3$, is also known, and is a colourless liquid, b.pt. $220°$. $SiHF_3$ (b.pt. $-97\cdot5°$), $SiHF_2Cl$ (b.pt. $ca-50°$) and $SiHFCl_2$ (b.pt. $-18°$) are obtained by fluorinating silicochloroform with antimony trifluoride. $SiCl_4$, by a similar reaction, gives rise to SiF_4, SiF_3Cl, SiF_2Cl_2 and $SiFCl_3$; all these compounds are gaseous at ordinary temperatures, except $SiFCl_3$, which boils at $12\cdot2°$. Partially chlorinated silanes, such as SiH_3Cl and SiH_2Cl_2, may also be fluorinated, when SiH_3F and SiH_2F_2 are obtained. Germanium chloroform is a liquid (b.pt. $75\cdot2°$, m.pt. $-71°$) which corresponds to silicochloroform in all respects; it can be obtained by the union of $GeCl_2$ and HCl. GeH_3Cl, GeH_2Cl_2, GeH_3Br, GeH_2Br_2 and $GeHBr_3$ have also been prepared.

The partly halogenated products which are formed from B_2H_6 and bromine, or better, chlorine, are not very stable, but decompose easily into the hydride and halide, e.g. B_2H_5Br forms BBr_3 and B_2H_6 (see p. 769). For this reason the investigation of these compounds is very difficult. The compound B_2H_5I can be prepared by the reaction: $B_2H_6 + HI \longrightarrow B_2H_5I + H_2$. It is a colourless liquid freezing at $-110°$ and gives a "Wurtz" reaction with sodium amalgam: $2B_2H_5I + 2Na \longrightarrow B_4H_{10} + 2NaI$. This method of formation of B_4H_{10} confirms the constitution given on p. 773. For B_2H_5Cl, which is important for the preparation of B_2H_6, see p. 765. The silicon compounds are much more stable than the boron compounds; they may be kept practically unchanged, particularly when rich in halogen, the chlorine compounds being more stable than those which contain bromine. $SiHCl_3$ is decomposed only at a red heat, when a reversible equilibrium is established: $4SiHCl_3 \rightleftharpoons Si + 3SiCl_4 + 2H_2$. All these compounds are colourless. In their chemical behaviour they retain many properties of the pure hydrogen compounds, and whereas the carbon compounds only react sluggishly, the silicon and boron compounds are capable of the greatest activity, being spontaneously inflammable in the air, or at least on touching the mixture with air with a warm object; $SiHCl_3$ and $SiHBr_3$ even detonate and give bright flames. Moreover, water decomposes them immediately—though $SiHCl_3$ needs a somewhat longer time—and they therefore fume strongly in moist

[1] Stock and Somieski, *Ber.*, 1917, **50**, 1739.

air. The decomposition of B_2H_5Br gives boric acid with elimination of hydrogen:

$$B_2H_5Br + 3H_2O \longrightarrow B_2O_3 + HBr + 5H_2,$$
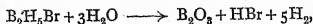
and is thus very similar in properties to the hydrides of boron. The decomposition of the halogenated silanes is especially interesting, since here the halogen is easily exchanged for oxygen, and a compound belonging to the siloxane group (see p. 832) is formed:

$$2SiH_3Cl(Br) + H_2O \longrightarrow (SiH_3)_2O + 2HCl(Br),$$
$$SiH_2Cl_2(Br_2) + H_2O \longrightarrow (SiH_2O)_x + 2HCl(Br),$$
$$2SiHCl_3 + 3H_2O \longrightarrow Si_2H_2O_3 + 6HCl.$$
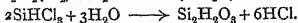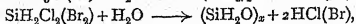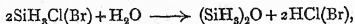
On the other hand, they form SiO_2 or hypoborate with alkali, like the pure hydrogen compounds (p. 840). By using zinc methyl, $Zn(CH_3)_2$, the chlorine can be replaced by methyl:

$$2SiH_3Cl + Zn(CH_3)_2 \longrightarrow 2SiH_3 \cdot CH_3 + ZnCl_2.$$
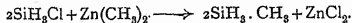
$SiHCl_3$ dissolves without decomposition in CS_2, CCl_4, C_6H_6, etc.; its relationship to carbon compounds is shown by the fact that it can dissolve paraffin when warm. The iodo-derivatives SiH_3I (b.pt. $45\cdot4°$) and SiH_2I_2 (b.pt. $149\cdot5°$) though they burn readily are not spontaneously inflammable in air.

Completely Halogenated Products.—The formulae of the completely halogenated compounds of this group can generally be derived from the ordinary valency of the elements. Chain compounds corresponding to the hydrogen compounds are known only for carbon and silicon; boron does not give them, for B_2Cl_6 decomposes immediately into $2BCl_3$. Direct combination of carbon and fluorine gives CF_4, C_2F_6, C_3F_8, etc., to C_7F_{16}, together also with an ethylene analogue C_2F_4; these products are gaseous and can be separated by fractional distillation. They are extremely stable to heat and to most reagents and are not attacked by sodium at moderate temperatures. A grey solid, CF, is obtained by the interaction of graphite and fluorine at atmospheric pressure at $420°$. It is insoluble in most reagents, but zinc and acetic acid regenerate graphite. X-ray analysis[1] shows that the distances between the carbon atoms in the basic planes are practically unaltered, but that the distances between the planes is increased from $3\cdot41$ Å to $8\cdot17$ Å (see Fig. 19, p. 21) by the insertion of fluorine atoms (see also p. 143). The silicon halides are formed by acting on silicon tetrahalide with excess silicon: $3SiCl_4 + Si \longrightarrow 2Si_2Cl_6$ and for this reason are often found mixed with silicon tetrahalide, when this is prepared from silicon and halogen, as free silicon is always present at first. The fluoride is made by the action of ZnF_2 on the chloride. The iodo-compound Si_2I_6 may also be synthesised thus: $2SiI_4 + 2Ag \longrightarrow Si_2I_6 + 2AgI$.

[1] Ruff, Bretschneider and Ebert, *Z. anorg. Chem.,* 1933, **210**, 173.

The best-known compounds are:

Si_2F_6 (b.pt. $-19\cdot1°$)	Si_2Cl_6	Si_2Br_6 (b.pt. $240°$)	Si_2I_6 (m.pt. $250°$)
$(SiCl)_x$	Si_3Cl_8		SiI_2.
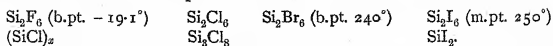
These are colourless compounds (with the exception of $(SiCl)_x$, a yellow solid, and SiI_2, which is orange red). They are split up at high temperatures, when e.g. Si_2Cl_6 forms Si and $SiCl_4$ slowly at $300°$, and quickly at $800°$. Si_2I_6 gives SiI_4 and SiI_2. They are easily decomposed by water, and therefore fume in air. Their hydrolysis leads to interesting products, in which the links between the silicon atoms themselves survive (cf. p. 833):

$$Cl_3Si-SiCl_3 + 4H_2O \longrightarrow 6HCl + HO_2Si-SiO_2H \text{ (silico-oxalic acid)},$$

$$Cl_3Si-SiCl_2-SiCl_3 + 5H_2O \longrightarrow 8HCl + HO_2Si-SiO-SiO_2H \text{ (silico-mesoxalic acid)}.$$
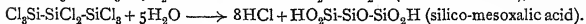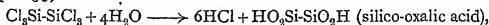
Controlled hydrolysis of $(SiCl)_x$ gives red $(SiOH)_x$ at low temperatures, otherwise yellow $Si_4(OH)_6$.

The halogen compounds which contain only one central atom are the most easily obtained—$BF_3(Cl_3, Br_3, I_3)$, $SiF_4(Cl_4, Br_4, I_4)$, etc. Those which are derived from the more metallic elements of this group have already been discussed on p. 326 et seq. The carbon compounds are distinguished by their greater stability, particularly towards water, while in their general properties they fall into line with the other tetrahalides. This may be seen from the following table, which may be supplemented by that on p. 325:

		Fluoride.	Chloride.	Bromide.	Iodide.
B	M.pt. .	$-127°$	$-107°$	$-46°$	$+43°$
	B.pt. .	$-101°$	$12\cdot5°$	$90\cdot3°$	$210°$
C	M.pt. .	?	$-23\cdot8°$	$92\cdot5°$	?
	B.pt. .	$-150°$	$76\cdot7°$	$189°$	?
Si	M.pt. .	$-77°$ (2 atm.)	$-68\cdot7°$	$+5°$	$120\cdot5°$
	B.pt. .	$-90°$ (subl.)	$56\cdot9°$	$153\cdot4°$	ca. $290°$

Silicon isocyanate (m.pt. $26\cdot0°$, b.pt. $185\cdot6°$) can be obtained in 98 per cent. yield by refluxing a suspension of silver isocyanate with silicon tetrachloride in benzene. Some cyanate is produced at the same time.[1]

The compounds are all colourless except CI_4, which is dark red. Their preparation is similar to that of the tetrahalides of the more metallic elements (p. 323): either from halogen and elementary boron, silicon, etc., or from halogen and the oxides, which are active when a third element is present to take up the oxygen of the oxide, e.g. carbon. Instead of the free halogens, compounds like CCl_4, S_2Cl_2, $HgCl_2$, $PbCl_2$, AsF_3, BF_3, etc., can be used. Direct reaction between the oxide and the halogen hydride occurs only when hydrogen fluoride is used:

$$B_2O_3 + 6HF \longrightarrow 2BF_3 + 3H_2O \qquad SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O.$$

This convenient method of preparation is carried out by mixing the

[1] Forbes and Anderson, J. Amer. Chem. Soc., 1940, 62, 761.

oxide (sand, glass) with fluorspar (CaF_2) and concentrated sulphuric acid.

The chemical properties are also similar to those of the tetrahalides of the more metallic elements. The most striking property is that of fuming in the air. Their ability to form compounds with ammonia and other gases is worthy of note: boron bromide, for example, forms addition compounds with ammonia as well as with PCl_3, PCl_5, $POCl_3$, AsH_3, etc.; nitric oxide and NOCl can also be added on to many of these halides. SiF_4 gives $SiF_4 . 2NH_3$ by heating silicates with ammonium fluoride; silicon tetrachloride forms addition products with ammonia at low temperatures, which undergo decomposition on warming (cf. p. 636).

Boron fluoride forms addition compounds with sulphates and phosphates, e.g. K_2SO_4, BF_3; $Cs_2SO_4, 2BF_3$; $K_2P_4O_7, 4BF_3$; K_3PO_4, BF_3. These compounds are decomposed by water.[1]

Mixed halogen compounds also exist, but can merely be referred to here; the fluorochlorides SiF_3Cl, SiF_2Cl_2, etc., are formed when chlorine reacts with Si_2F_6, which in turn is obtained from Si_2Cl_6 and Z_nF_2. SiF_3Br, SiF_2Br_2 and $SiFBr_3$ also exist, while Schumb and Anderson[2] have prepared $SiFClBr_2$ and $SiFCl_2Br$. All the mixed fluorochlorides corresponding to germane are also known. The following survey gives the melting and boiling points of some of the silicon compounds:

	$SiCl_3Br$	$SiCl_2Br_2$	$SiClBr_3$	$SiCl_3I$	$SiCl_2I_2$	$SiClI_3$	$SiBr_3I$	$SiBr_2I_2$	$SiBrI_3$
M.pt.	...	...	−39°	...	...	2°	14°	38°	53°
B.pt.	80°	104°	127°	114°	172°	236°	192°	230°	255°

$K_2B_2F_6 . 1\tfrac{1}{2}H_2O$ is obtained from KHF_2, boric acid and water, and if KBF_4 is heated at 580°, $K_4B_4F_{10}$ is obtained.[3]

Structural formulæ corresponding to these are :
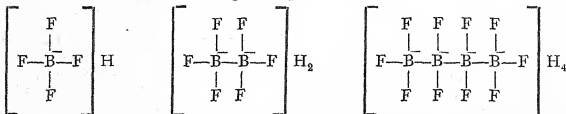
Complex Fluorine Acids.—The halides of Sn, Pb and other quadrivalent elements (p. 323) readily form complex halogen acids. This property falls off with decrease in atomic weight. It is not found in C, and only to a restricted extent in B and Si, in which the fluorides form very stable fluoro-acids with HF, although analogous chloro-acids do not occur :

$$BF_3 + HF \longrightarrow [BF_4]H \qquad SiF_4 + 2HF \longrightarrow [SiF_6]H_2.$$
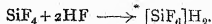
[1] Baumgarten and Hennig, Ber., 1939, 72, 1743.
[2] See Schumb and Gamble, J. Amer. Chem. Soc., 1932, 54, 3943 ; Booth and Swinehart, ibid., 1932, 54, 4750 ; J. Amer. Chem. Soc., 1937, 59, 651.
[3] Travers and Malaprade, Bull. Soc. chim., 1930, iv., 47, 788.

The atomic volume of boron and silicon is possibly too small for the requisite number of 4 or 6 chlorine or bromine atoms to arrange themselves round it so as to be sufficiently near to the central atom.

Hydrofluoboric and hydrofluosilicic acids correspond in their properties to the hydrofluoric acids of the quadrivalent metals, such as H_2TiF_6, H_2ZrF_6, H_2SnF_6 (p. 329 *et seq.*), and their salts are often isomorphous with those of these acids.

These acids may be prepared synthetically if BF_3 or SiF_4 is passed into a solution of hydrofluoric acid. Synthesis does not take place in the gaseous state, as the acids are then very largely decomposed.[1] It is found, however, that if SiF_4 or BF_3 is passed into water, hydrogen fluoride is formed by hydrolysis and can then combine with a further quantity of the fluoride. Silicic acid or boric acid is also obtained: $SiF_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HF$ and $SiF_4 + 2HF \longrightarrow H_2SiF_6$; hence the liquid contains H_2SiF_6 as well as gelatinous silicic acid, which is deposited. The hydrofluoboric acid is prepared in a similar way.

Both acids are fairly strong. They are not known in the anhydrous state, but a crystalline dihydrate of hydrofluosilicic acid is known (m.pt. 19°) and possibly a tetrahydrate as well (m.pt., 0°). Concentration of these acids by evaporation results in partial decomposition; a hydrofluosilicic acid containing 13.3 per cent. can be distilled without decomposition, but more concentrated acids undergo dissociation, and more SiF_4 passes over than corresponds with the formula, while, on the other hand, more HF volatilises from weaker acids. For this reason the concentrated acid attacks glass, as it contains free hydrofluoric acid; the more dilute acid does not do this, but deposits silicic acid, as it contains free SiF_4. The behaviour of the hydrofluoboric acid is very similar. Solutions of hydrofluosilicic acid containing more than 13.3 per cent. can be obtained by passing SiF_4 into water. They are colourless liquids which fume only at high concentrations, and have the following densities:

Concentration .	10	20	30	34%
Density . .	1.083	1.175	1.274	1.316

Molecular weight determinations show that the free acid is greatly decomposed in the state of vapour. KBF_4 in solution gives a definitely acid reaction, since the BF_3 formed by its decomposition hydrolyses, but the dry silico- and boro-fluorides may be subjected to very high temperatures without giving off SiF_4 or BF_3, provided they are protected from atmospheric moisture. If this is not done, they are hydrolysed at red heat, and the metal fluoride or oxide is left. Concentrated alkali also decomposes them completely, as the small quantities of the free acids present are removed, according to the equation $H_2SiF_6 + 6KOH \longrightarrow 6KF + Si(OH)_4 + 2H_2O$.

[1] C. A. Jacobson, *J. Phys. Chem.*, 1923, **27**, 761 ; 1924, **28**, 506.

Only the normal salts of hydrofluosilicic acid are known. Their properties are those of the salts of an acid having a somewhat bulky anion; they thus resemble the salts of chloroplatinic acid, perchloric acid and similar compounds. The alkali salts crystallise in the regular system, and like those of the acids mentioned they are difficultly soluble. Further, the alkali salts are anhydrous, while those of the alkaline earths (and of lithium) mostly contain 2 molecules of water, and are much more soluble. The lead, silver and copper salts contain 4 mols. H_2O, and the salts with the smallest cations (those of the bivalent metals Ni, Co, Fe, Cd, Mg, Zn, Mn, Hg) all contain 6 mols. water, and are very soluble. Some of the salts of the rare earths and of aluminium are insoluble powders or jellies, but they have not yet been fully investigated. The potassium and sodium salts also separate in the gelatinous condition, the potassium salt in a form so finely divided that at first it is almost invisible, and then is gradually noticeable by the iridescence of the liquid. It gives the impression that it is a colloidal substance, but well-formed crystals are seen under the microscope—probably these are a transformation product of the first form. The barium salt is also difficultly soluble, but is deposited straight away in crystals. In alcohol the solubility of these salts is exceedingly low, e.g. that of the barium salt in 50 per cent. alcohol is 1 : 40,000. In water, at 17·5°, the solubilities of the silicofluorides are:

	Na	K	Rb	Cs	Ba
1 part in	153	833	620	166	3700 parts of water.

The existence of an ammonium compound, $(NH_4)_3SiF_7$, is remarkable; it resembles the zirconium compound described on p. 329 in its high co-ordination number.

The salts of hydrofluoboric acid resemble generally those of hydrofluosilicic acid. Here also the potassium salt is gelatinous, but on recrystallisation yields a second form in brilliant crystals. The other salts are easily soluble. There is some analogy between the salts of this acid and those of perchloric acid (cf. $HClO_4$, HBF_4).[1] The general property of perchloric acid of precipitating organic bases is paralleled in hydrofluoboric acid, but quinidine is precipitated from acetic acid solution by neither of these acids.

Oxyfluoboric Acids.—In one respect BF_3 behaves differently from SiF_4 when passed into water—with an excess of the fluoride the boric acid originally formed is again attacked, and the hydrogen fluoride evolved combines with the boric acid to form oxyfluoboric acid, i.e. $BF_3 . 2H_2O$. This compound, and also $BF_3 . H_2O$, are obtained[2] by the combination of BF_3 and H_2O. According to Herz,[3]

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[1] E. Wilke-Dörfurt and G. Balz, *Ber.*, 1927, 60, 115.

[2] Meerwein, *Ber.*, 1933, 66B, 411; Meerwein and Pannwitz, *J. pr. Chem.*, 1934, ii. 141, 123.   [3] *Abegg-Handb.*, iii. 1, 22.

they may possibly be compared to the acid, $H_2[PtCl_4(OH)_2]$, prepared from $PtCl_4$ and H_2O (p. 329), $BF_3 \cdot H_2O$ is formulated as $H[BF_3(OH)]$. It is formed when BF_3 is passed into water to saturation, and is a fuming oil, similar to concentrated sulphuric acid even in its corrosive and carbonising properties. On heating it yields BF_3. It is apparently able to form salts, since when potassium fluoride is added to aqueous boric acid the solution becomes alkaline, which may be represented as a result of the hydrolysis of the potassium salt of the oxyfluoboric acid produced, since that acid is weak. Its salts are not known in the crystalline condition, but salts of a peroxyfluoboric acid crystallise out on the addition of hydrogen peroxide. The acid $H[BF_2(OH)_2]$, b.pt. 159°, is obtained[1] by the interaction of B_2O_3 and HF.

OXYGEN COMPOUNDS OF THE ELEMENTS OF GROUP IV

Of the oxygen compounds of this group only the dioxides of the elements of higher atomic weight have a considerable resemblance to each other. The other oxides possess such specific properties that they must be discussed singly. Those formed by carbon are distinct from the rest on account of their lack of polymerisation; they are gaseous while all the others are highly polymerised, and are difficult to depolymerise even by heating, and are therefore extraordinarily non-volatile. The unsaturated compound corresponding to one of the oxides of carbon, CO, is completely lacking in silicon and boron, but occurs again in the heavier elements, when it has the properties of a true metallic oxide, while the dioxides of these elements have at least amphoteric properties, but tend to give acids rather than bases.

The Oxides of Carbon

The following three oxides of carbon are known :

$$C_3O_2 \qquad\qquad CO \qquad\qquad CO_2.$$
Carbon suboxide. Carbon monoxide. Carbon dioxide.

Carbon suboxide, $O : C : C : C : O$, is formed from malonic ester by dehydration with phosphorus pentoxide :

$$CH_2(CO_2C_2H_5)_2 \longrightarrow 2C_2H_4 + 2H_2O + C_3O_2,$$
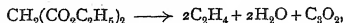
and is also produced by the action of the silent electric discharge on carbon monoxide[2]: $4CO \longrightarrow C_3O_2 + CO_2$. It is best obtained by heating[3] diacetyltartaric anhydride. It is a gas which condenses to a colourless liquid at 7°, and solidifies[4] at $-111°$. Electron diffraction experiments show the C_3O_2 molecule to be linear, and furthermore the carbon-carbon distances are 1.30 Å and the carbon-oxygen distances

[1] Sowa, Kroeger and Nieuwland, *J. Amer. Chem. Soc.*, 1935, 57, 454.
[2] Ott, *Ber.*, 1925, 58, 772.
[3] Hurd and Pilgrim, *J. Amer. Chem. Soc.*, 1933, 55, 757.
[4] Diels, *Ber.*, 1906, 39, 689.

1·20 Å. This shows a considerable shortening of the usual interatomic distances required by $O=C=C=C=O$ and indicates that C_3O_2 is a resonance hybrid,[1] to which the structure $: \overset{+}{\ddot{O}}=C-C\equiv C-\ddot{O}:$ and $: \ddot{O}-C\equiv C-C\equiv \overset{+}{\ddot{O}}$ each contribute about 20 per cent. and the structure $O=C=C=C=O$ most of the remaining 60 per cent. Similarly pentacarbon dioxide (b.pt. about 105°), the existence of which is uncertain, may be a resonance hybrid.

Formation and Equilibrium of Carbon Monoxide.—Carbon monoxide and carbon dioxide are formed in the combustion of carbon (for other modes of formation see pp. 780 and 796), the former in the presence of an excess of carbon and the latter in an excess of oxygen. Carbon monoxide itself can be burnt to carbon dioxide in an excess of oxygen, but without the addition of oxygen it can also undergo decomposition into carbon and carbon dioxide on heating to a higher temperature. Carbon dioxide can likewise be decomposed on heating into carbon monoxide and oxygen. In the system carbon-oxygen there are thus two irreversible processes:

$$2C + O_2 \longrightarrow 2CO \qquad \text{and} \qquad C + O_2 \longrightarrow CO_2,$$
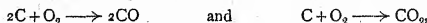
as well as two reversible reactions:

$$2CO_2 \rightleftharpoons 2CO + O_2 \qquad \text{and} \qquad 2CO \rightleftharpoons C + CO_2,$$
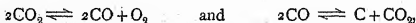
and therefore six possible reactions. Of these, the direct process $C + O_2 \longrightarrow CO_2$ is very difficult to realise. In consideration of the great significance which the oxidation of carbon has for the combustion of fuel and for reduction processes, great pains have been taken to place the relations of this system on a firm basis.

The heat changes in the individual reactions are as follows:

$$C + O_2 \Longrightarrow CO_2 + 97\cdot8 \text{ Cal.} \qquad 2C + O_2 \longrightarrow 2CO + 59\cdot2 \text{ Cal.}$$
$$2CO + O_2 \longrightarrow 2CO_2 + 136\cdot4 \text{ Cal.} \qquad 2CO \longrightarrow C + CO_2 + 38\cdot75 \text{ Cal.}$$
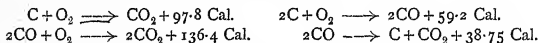
From a knowledge of these, however, it cannot be decided which process is the one most favoured under definite conditions, as Berthelot's Law states for such systems that the reaction which takes place is not that which gives the greatest evolution of energy, but that which gives it at a temperature so low that in consequence of the small reaction velocity then prevailing an exchange is not accomplished. The dependence of the equilibrium on temperature (and on pressure) can be confirmed by measurement of the equilibrium constant at different temperatures. By calculation, the effect of temperature and pressure on the equilibrium can then be established. The energy liberated by each of the four reactions, at all possible temperatures, is known, especially from the investigations of Haber and Nernst and

[1] Pauling and Brockway, *Proc. Nat. Acad. Sci.*, 1933, 19, 800 ; Boersch, *Monatsh.*, 1935, 65, 311 ; Thompson and Linnett, *J. Chem. Soc.*, 1937, 1291.

their pupils. Expressed in large calories, examples of these are as follows:

$$\text{(1) } C + O_2 \longrightarrow CO_2 \qquad \text{(2) } 2CO + O_2 \longrightarrow 2CO_2$$

	At 17°			96·6	123·8 Cals.
	„ 1500°	.	.	91·5	60·2 „

$$\text{(3) } 2C + O_2 \longrightarrow 2CO \qquad \text{(4) } C + CO_2 \longrightarrow 2CO$$

	At 17°			69·5	− 28·9 Cals.
	„ 1500°	.	.	122·6	+ 35·2 „
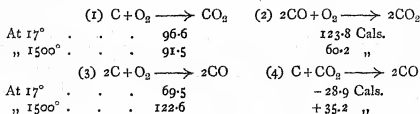
With rise in temperature the change in these quantities of energy is almost linear. Of the first three reactions the heat evolution in (2) is the highest at lower temperatures and the lowest at higher temperatures, while the third behaves in the reverse manner. Hence in the equilibrium between carbon and oxygen, CO_2 preponderates at lower and CO at higher temperatures.

The energy of the reaction (1), in contrast to these, is dependent only slightly on the temperature—it falls a little at higher temperatures. There is a point about 690° where all three reactions have the same energy value. The energies of all three reactions are always positive at all accessible temperatures, whilst reaction (4) has a negative energy at lower temperatures, so that it cannot then take place, but free carbon and CO_2 are formed from CO, a reaction which is only reversed at higher temperatures, when the energy of the reaction becomes positive.

In the combustion of carbon in air, according to Boudouard,[1] CO and CO_2 are formed in the following proportions:

	500°	600°	700°	800°	900°
Per cent. CO .	7·1	9·7	23·1	29·9	34·0
Per cent. CO_2 .	16·7	15·1	6·9	2·8	0·2

These reactions, as usual, slow down to a great extent at low temperatures; the spontaneous decomposition of CO into C and CO_2, for example, is not noticeable at ordinary temperatures. At higher temperatures a catalyst is required in order that the position of equilibrium may be quickly attained, and the metals iron, cobalt and nickel are best suited for the purpose. Here the metallic iron itself does not act as a catalyst, but only its carbide, Fe_3C; until this synthesis is accomplished with the aid of the separated carbon the reaction only takes place slowly. It is interesting to note that the carbon separates out as a deposit in the graphitic or less compact form, in agreement with the observations made on p. 138 on the mode of formation of its different modifications. The equilibrium between CO and CO_2 caused by such a catalyst corresponds to the following percentages of CO_2:

% CO_2	·98	89·3	61	25	6	1·5	0·34
At	450°	550°	650°	750°	850°	950°	1050°

[1] Ann. Chim. Phys., 1901 [7], 24, 5.

The proportions are easily measured if the gaseous mixture is withdrawn quickly from the region of high temperature.

The equilibrium of the reaction (2), $2CO_2 \rightleftharpoons 2CO + O_2$, may be observed with somewhat greater difficulty on rapid cooling. In order to elucidate it the following methods have been used: vapour density estimation; the analysis of gases from CO-O_2 flames by leading them away by the introduction of a small tube at various points; the hot and cold pipe method, in which the gas mixture, streaming very quickly through a hot pipe, arrives at a cooler zone in a narrow capillary; the method in which the gas mixture is passed over a thin electrically heated wire, the fall of temperature in the gas space away from the wire being sufficient to cool the products and fix the equilibrium mixture, while the temperature of the wire is obtained by measurement of resistance, etc. The most reliable experimental results are those of Nernst and v. Wartenberg,[1] who used the method of streaming through a tube, and those of Langmuir,[2] who worked with the hot wire method. According to the former the decomposition of carbon dioxide under atmospheric pressure is as follows:

T.	290°	1000°	1200°	1400°	1600°
Per cent.	$8 \cdot 2 \times 10^{-30}$	$1 \cdot 6 \times 10^{-5}$	$8 \cdot 9 \times 10^{-4}$	$1 \cdot 38 \times 10^{-2}$	0·104
T.	1800°	2000°	2200°	2400°	2500°
Per cent.	0·507	1·77	4·88	11·3	15·8

Under diminished pressure the dissociation of the carbon dioxide is naturally greater, since the reaction is accompanied by an increase in volume. At 2500° T. the percentage decomposition of carbon dioxide is:

Atm. pressure	0·01	0·1	1	10
Per cent. CO_2 decomp.	53	30·7	15·8	7·08

The reaction $2CO + O_2 \longrightarrow 2CO_2$ may take place with explosion. It has been specially well studied by Dixon (cf. also p. 391), including the phenomena of the explosion velocity, the course of the explosion waves, the explosion temperature, etc. The explosion temperature, i.e. that which is necessary as a minimum for the explosion to begin, is obtained most exactly by subjecting the gas mixture to sudden compression, so that the explosion is induced by the heat of compression. The temperature produced by this gas compression can be calculated, and it is possible in this way to explode the gas mixture at a uniformly raised temperature more quickly than by any other method, without being afraid of heat radiation outside or the slow induction of the reaction in the region of higher temperature.[3] The explosion temperature in this way is found to be 601°. It is noteworthy that this explosion occurs only if the gases are not

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[1] Z. physikal. Chem., 1906, 56, 548.   [2] J. Amer. Chem. Soc., 1906, 28, 1357.
[3] Falk, Ann. Phys., 1907, 24, 471.

dry.[1] Otherwise the combination is very gradual, *e.g.* if the gas mixture is passed over a heated platinum sponge, or if a glowing platinum spiral is introduced, when the heat of reaction is sufficient to maintain the spiral at red heat. Even a burning mixture of carbon monoxide and oxygen is immediately extinguished if dried gases are supplied, as the temperature of the flame is then insufficient to promote the reaction rapidly enough to maintain the ignition temperature. In the presence of very small quantities of water explosions are possible but these proceed with a low velocity, and the explosion velocity probably depends directly on the amount of water present. The action is due to the addition of water, with the production of formic acid : $CO + H_2O \longrightarrow HCOOH$, the synthesis and decomposition of which occurs at a lower temperature than is necessary for the direct union of CO and O_2.[2] Water is not the only substance which acts in this way in causing explosions, for other gases containing hydrogen, *e.g.* H_2S, NH_3, C_2H_4, etc., also catalyse the reaction, when hydrogen-free gases like SO_2, CO_2, N_2O, etc., have no effect. Mixing with greater quantities of foreign gases reduces the speed of the explosion, since they act as "buffers." The effect of water on chemical reactions has been considered previously (*cf.* p. 394); but with reactions of gases other than CO, the explosion when it occurs in absence of water, is made slower by the presence of water, *e.g.* in hydrogen and oxygen or hydrogen and chlorine ; the $CO - N_2O$ explosion is, however, assisted by water. There are also methods of preparation of CO_2 which do not necessitate the presence of water, *e.g.* the burning of cyanogen in oxygen in the completely dry state.[3] The union of CO and O_2 and that of H_2 and O_2 when caused by the action of ultra-violet light, is likewise independent of the presence of moisture.[4]

It might be expected that ozone would oxidise carbon monoxide more readily than ordinary oxygen ; the reaction does not, however, take place quickly, but may be accelerated by illumination with ultra-violet light.

The Water-Gas Equilibrium.—The heat evolved in the burning of coal may be made use of directly, but it is often preferable to conduct the heating process at a place other than the spot where combustion of the coal is carried out. This advantage is obtained by the so-called gasification of coal, which may be carried to completion by the use of atmospheric oxygen, when carbon monoxide is generated by the reaction $C + O \longrightarrow CO$, led to the desired spot and there burnt to CO_2. The CO, naturally, is mixed with atmospheric nitrogen (*producer gas*). *Water-gas* is free from such substances, which act as diluents and absorbers

[1] For a general summary see W. A. Bone, *J. Chem. Soc.*, 1931, 338.
[2] Wieland, *Ber.*, 1912, 45, 679 ; *cf.* p. 391.
[3] Dixon, *Ber.*, 1905, 38, 2419.
[4] Coehn and Tramm, *Ber.*, 1921, 54, 1148; 1923, 56, 455.

of heat, and is obtained by treating red-hot coke with steam. The gasification of the carbon ensues by means of the oxygen contained in the water, and may result either from (1) $C + H_2O \longrightarrow CO + H_2$ or from (2) $C + 2H_2O \longrightarrow CO_2 + 2H_2$. In the production of water-gas two processes take place concurrently: first, the exothermic oxidation of the carbon to CO and CO_2 respectively; and secondly, the endothermic decomposition of the water into 2H and O. The oxygen of the water can only act as an oxidant after it is liberated from the water, and since the heat of decomposition of water is greater than the heat of combustion of the carbon to CO, the formation of water-gas is a process which on the whole absorbs heat. It can therefore only be completed if, as a preliminary reaction, some of the carbon is burnt in air. The reaction (1) above takes place with ease above 1200°; below this temperature reaction (2) commences, and below 1000° proceeds alone. It is found from experience in the production of water-gas that the burning of the coke must first be started by blowing in air; then the air is replaced by steam, whereupon water-gas is formed by the endothermic reaction. As soon as the mass has cooled too far it must again be heated by blowing in air. In this way the preparation is an intermittent process. The first part, the heating of the coke, may be carried out in various ways: either the formation of CO is aimed at, when producer gas is obtained; or the formation of CO_2, when the products of combustion of this first phase cannot be used any further. Yet this last method is the more economical, since a higher temperature is generated from the reaction (Dellwik-Fleischer). Also, while the coke is cooling down, the conditions are more suitable for reduction of the first CO_2 generated, and this is converted into CO by the coke present.

On account of the importance of water-gas as a fuel it is desirable to note the relations between its components, which are given by the equilibrium $\dfrac{H_2O \times CO}{CO_2 \times H_2} = K$. The equilibrium constants K are as follows:

Temp.	686°	830°	986°	1205°	1500°	1600°
K	0·52	1·0	1·60	2·60	3·87	4·24

At temperatures lower than 830°, CO is a stronger reducing agent than hydrogen, since in the competition between equimolecular quantities of CO and hydrogen for the oxygen present, more CO_2 than H_2O is formed. At temperatures above 830°, on the other hand, hydrogen reduces more readily than carbon monoxide. It is also interesting and important to examine the energy content and the reactions between elementary carbon and water, which can give rise either to carbon monoxide or to carbon dioxide. This was first done by Horstmann and later by many other investigators—most completely

by Hahn.[1] Here again a linear change of the energy of reaction with temperature was found, as in the C—CO—CO_2—O_2 equilibrium. The energy of the reactions is as follows:

$$2CO + 2H_2O \longrightarrow 2CO_2 + 2H_2 \qquad C + 2H_2O \longrightarrow CO_2 + 2H_2$$

17°:	15·94 Cal.	− 11·2 Cal.
1500°:	9·79 Cal.	21·2 Cal.

$$2C + 2H_2O \longrightarrow 2CO + 2H_2$$

17°:	− 38·3 Cal.
1500°:	52·0 Cal.
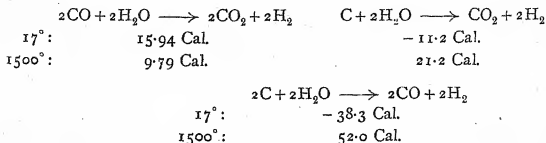
Only the first of the three reactions is spontaneous at lower temperatures, since it alone liberates energy under those conditions. Both the others need the addition of energy. This situation is, however, reversed at higher temperatures, when the first reaction proceeds least readily, while the third, the water-gas process, is the most exothermic.

The delay in the reaction $2CO + O_2 \longrightarrow 2CO_2$ at low temperatures may be so diminished by certain contact materials that it proceeds at ordinary temperatures. The combination occurs most readily in the presence of a catalyst of metallic copper moistened with alkali, which is best precipitated on retort carbon in order to obtain a rapid reaction. The reaction goes to completion with a peroxide of copper as an intermediate stage. As the chief evolution of energy in the conversion of carbon into carbon dioxide is in the reaction $2CO + O_2 \longrightarrow 2CO_2$, it would be very valuable to be able to carry it out without actual combustion, in which, on account of the imperfections of machinery, friction, radiation, etc., a very considerable part of the energy is always lost. This idea of converting the energy of coal into electrical energy without use of the dynamo is very old, and one of the possibilities of overcoming at least the technical difficulty of the oxidation of carbon monoxide is by the contact oxidation above.[2] If two copper electrodes are dipped into an alkaline liquid, and one is surrounded with air and the other with carbon monoxide to give a galvanic element:

$$-\boxed{O_2 \mid Cu \mid Alkali \mid Cu \mid CO}\,+,$$
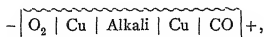
the oxidation of the carbon monoxide is completed inside this element, and the resulting current can be utilised. The E.M.F. is 1·32 volts. In other similar elements Weldon mud is used as oxygen carrier at the cathode, as it can be regenerated by blowing in air. The use of these and similar combustible elements is chiefly frustrated by the slowness with which the reaction is completed, so that the amount of current developed in unit time is very small.

[1] Z. physikal. Chem., 42-45.
[2] Hofmann, Ber., 1915, 51, 1526.

With the help of oxidising agents stronger than molecular oxygen the oxidation of carbon monoxide is more rapid, and that of carbon itself also takes place if the element is finely divided. Yellow mercuric oxide is reduced by CO at room temperature, and silver oxide gives the metal at $-21°$. Iodine pentoxide, also, is reduced at a moderate temperature. Carbon monoxide is thus a more powerful reducing agent than hydrogen. Compounds of gold and of the platinum group are also reduced to metal by CO at ordinary temperatures, only rhodium compounds requiring a slightly higher temperature. Permanganate oxidises CO most quickly in the presence of finely divided metallic silver, and chromic acid is such an excellent oxidising agent in the presence of mercury salts that it may be used in gas analysis. The behaviour of chlorates is noteworthy: they oxidise CO only in the presence of osmium tetroxide, though carbon monoxide is usually so powerful a poison for catalysts that its presence, even in the smallest traces, can be recognised by the retardation of reactions which proceed catalytically (Hofmann).

It is curious that some bacteria can oxidise CO to CO_2; and this gas, so fatal to human beings, is not deadly to green plants or to the bacteria of humus soils. When left over damp garden soil CO disappears completely with formation of CO_2 if oxygen is available, otherwise with production of H_2S, the sulphur being derived from the sulphates present.[1]

Apart from the combustion of carbon (or of carbides), carbon monoxide and dioxide are formed by the elimination of water from those organic compounds which may be regarded as hydrates of carbon monoxide or dioxide. Such a compound is oxalic acid, $H_2C_2O_4$:

$$\begin{array}{c} COO \;\vdots H \\ \cdots | \cdots \\ CO \;\vdots OH \end{array}$$
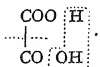
Water is removed by warming with concentrated sulphuric acid, the CO_2 and CO escape, and pure CO can be obtained by removing the CO_2 from the gas mixture by potassium hydroxide solution. Pure CO may also be obtained by the dehydration of formic acid,

$$O = C \Big\langle \begin{array}{c} OH \\ H \end{array},$$
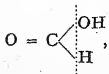
by means of concentrated sulphuric acid or by the similar treatment of cyanides (ferrocyanides, potassium cyanide), since hydrocyanic acid is the nitrile of formic acid; it is first converted to formic acid and then dehydrated.

[1] Wehmer, *Ber.*, 1926, 59, 887.

Properties of Carbon Monoxide.—Carbon monoxide is a colour-less, odourless gas with well-known poisonous properties. It may be condensed at $-190°$ to a colourless liquid, which solidifies $9°$ lower, and has a density of 0.79 at its boiling point. It is only slightly soluble in water: 0.00440 per cent. at $0°$ and 0.00279 per cent. at $20°$; it is somewhat more soluble in some organic liquids, but not to any great extent in any.

There are, however, certain salt solutions in which carbon monoxide dissolves much more easily. The absorption of carbon monoxide by the red colouring matter of blood, hæmoglobin, is physiologically important; among inorganic salts the compounds with univalent copper salts are important. Cuprous chloride solution is therefore used in gas analysis to absorb carbon monoxide; in hydrochloric acid or in ammoniacal solution it combines with a maximum of one molecule of the gas, and the crystalline compound $CuCl.CO.2H_2O$ can be obtained from the solution. Anhydrous cuprous chloride combines with CO under pressure,[1] but it can more readily be absorbed if water, ammonia or organic bases enter the molecule at the same time. Addition of carbon monoxide increases the stability of otherwise very unstable cuprous salts; e.g. a compound of cuprous sulphate, $Cu_2SO_4.2CO$, is formed if a solution of copper sulphate in contact with metallic copper is treated with CO. These cuprous-carbon monoxide com-pounds are generally not very stable, and show quite an appreciable dissociation pressure at ordinary temperatures.[2] For this reason a CuCl solution absorbs the CO from the gaseous region only in definite proportion, and to obtain complete absorption a fresh CuCl solution, containing no CO, must be brought into contact with the gas mixture at the end, after the greater part of the carbon monoxide has been absorbed. The compounds $CuCl.CO$ and $CuBr.CO$ have been shown to exist.

For a long time only a few addition compounds of CO were known, but Manchot has shown[3] that compounds of elements in a certain area in the periodic system—the sixth, the eighth and first groups and part of the second—can combine with CO, and such compounds have been isolated containing the following metals:

24 Cr	26 Fe	27 Co	28 Ni	29 Cu		
42 Mo	44 Ru	45 Rh	46 Pd	47 Ag		
74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg

Of the iron compounds, carboxyhæmoglobin has long been known. By removing the ammonia from the compound $[Fe(CN)_5NH_3]M_3$ (p. 310) by a stream of carbon monoxide, one obtains salts of the acid

[1] Wagner, *Z. anorg. Chem.*, 1931, **196**, 364.
[2] Manchot and Friend, *Ann.*, 1908, **359**, 100.
[3] *Ber.*, 1924, **57**, and following vols.

[Fe(CN)$_5$CO]H$_8$, which also appear in gas purifiers and are distinguishable by a deep violet colour reaction on addition of ferric chloride. Cobalt forms similar compounds.

Other CO addition compounds of bivalent iron: Fe(CO)$_5$X$_2$, Fe(CO)$_4$X$_2$, [Fe(CO)$_3$X$_2$]$_2$ were prepared by Hieber and Bader[1] whose work also throws some light on the constitution of these addition products. Fe(CO)$_2$X$_3$ and Fe(CO)$_3$X have also been described. If free halogen, X$_2$, is passed into a solution of Fe(CO)$_5$ in petroleum ether at $-8o°$, an addition compound Fe(CO)$_5$X$_2$ is formed, which easily loses CO and passes into Fe(CO)$_4$X$_2$. Excess of halogen does not give a ferric salt, nor can these compounds be made by using FeX$_3$ and CO. The stability of the chloride is less than that of the iodide addition compound and the formula [Fe(CO)$_4$]X$_2$ appears probable, though the above workers prefer [Fe(CO)$_4$X$_2$]. The compounds are decomposed by light, leaving behind FeX$_2$. Iron pentacarbonyl itself undergoes irreversible decomposition, at 0°. Water decomposes the addition compounds with removal of the CO, but the iodide reacts only slowly. Concentrated HCl also brings about decomposition, as do many oxygen compounds, amines, and ammonia. Pyridine decomposes the chloride and the bromide, but with the iodide the deep green Fe(CO)$_2$Py$_2$I$_2$ and the brown Fe(CO)Py$_2$I$_2$ are formed. Ammonia gas yields [Fe(NH$_3$)$_6$]X$_2$ at the ordinary temperature, but at $-2o°$ products are formed which still contain CO. Metallic mercury catalyses the elimination of CO, but the compound Fe(CO)$_3$I$_2$Hg$_2$ can be obtained from the more stable iodide. Hock and Stuhlmann[2] have isolated the compounds Fe(CO)$_7$HgCl$_2$ and Fe(CO)$_4$Hg$_2$Cl$_2$. The latter may be HgFe(CO)$_4$ HgCl$_2$. Fe(CO)$_5$ reacts with SbCl$_5$ and with SnCl$_2$ to form Fe(CO)$_4$SbCl$_5$ and Fe(CO)$_4$SnCl$_4$; the former is dissociated in benzene, but the tin compound, which is regarded as

$$(CO)_4Fe \underset{Cl}{\overset{Cl}{\diagdown}} Sn \underset{Cl}{\overset{Cl}{\diagup}} \quad \text{is unchanged.}$$
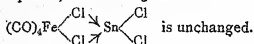
It would appear that CO and NO can at times, though rarely, replace one another. Thus Manchot found that the following equilibrium existed in the rhodium compounds:

$$RhCl_3 . RhO . 3CO + 3NO \rightleftharpoons RhCl_3 . RhO . 3NO + 3CO.$$
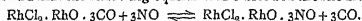
Co(CO)$_3$NO and Fe(CO)$_2$(NO)$_2$ are formed in the same kind of way, but Ni tends to form compounds of the [Ni(NO)]+ radicle, such as Ni(NO)OH. Nitrosyl halides, e.g. CO(NO)$_2$X, are also known. Among the nickel compounds the canary-yellow addition product, K$_2$[Ni(CN)$_3$CO], formed from the double cyanide K$_2$[Ni^i(CN)$_3$)] breaks up spontaneously into Ni(CO)$_4$ and Ni(CN)$_2$.

Elements of the lower series of Groups I and VIII in the periodic system give addition compounds of even simple salts and CO. Silver sulphate gives Ag$_2$SO$_4$. CO only in solution in concentrated sulphuric acid, but gold and the platinum metals give solid products. Some of these are unstable (Pd, Ir) but others are so stable that they may be sublimed unchanged (Pt, Os, Rh). Halide addition products are best known and have very varied formulae, e.g.

OsCl$_3$. 3CO	IrCl$_3$. 2CO ; IrX . 3CO	AuCl . CO
PtCl$_2$. CO	PtCl$_2$. 2CO	2PtCl$_2$. 3CO
RuCl$_3$. 2CO	RhCl$_3$. Rh . 3CO	RuBr . CO
PdCl$_2$. CO	PdCl$_2$. 2CO	2PdCl$_2$. 3CO

These substances are obtained by passing CO over the halide or over a higher halide. Most of them form white needles, but the basic rhodium compound is red and may be sublimed unchanged. Some of them can only be made in absence of water, for others traces of water or alcohol vapour are essential. Crystalline compounds of the type [Pt(CO)X$_2$]M, derived from PtCl$_2$, CO, are also known.

[1] Z. anorg. Chem., 1930, 190, 193.   [2] Ber., 1928, 61, 2097 ; 1929, 62, 2630.

Carbonyls.—Carbon monoxide forms addition compounds with metals, mainly with those of the eighth group of the periodic system. They are called metallic carbonyls and are not comparable with any other metallic compounds. Some of them are very easily volatilised.[1] They comprise the following compounds:

Monometallic Carbonyls

$Ni(CO)_4$	$Fe(CO)_5$	$Ru(CO)_5$
Colourless liquid.	Amber-yellow liquid.	Colourless crystals.
B.pt. 43°, m.pt. $-25°$.	B.pt. 103°, m.pt. $-21°$.	Very volatile, m.pt. $-22°$.

$Mo(CO)_6$ $Cr(CO)_6$ $W(CO)_6$ $Os(CO)_5$
Colourless crystals, very easily sublimed.

Polymetallic Carbonyls

$Fe_2(CO)_9$	$[Fe(CO)_4]_3$	$[Co(CO)_3]_4$	$[Co(CO)_4]_2$
Gold-coloured crystals.	Green crystals.	Black crystals.	Orange-coloured crystals.
Decomp. at 100°	Decomp. at 140°.	Decomp. at 60°.	M.pt. 51°, decomp. above 52 .

$[Re(CO)_5]_2$ $[Ru(CO)_4]_n$ $Ru_2(CO)_9$
Orange-yellow crystals.

$[Ir(CO)_3]_n$ $[Ir(CO)_4]_n$
Yellow crystals.   Greenish-yellow crystals.
Sublimes in CO at 250°-210°.   Sublimes in CO at 160°.

They are formed by the action of carbon monoxide on the finely divided metals. Nickel carbonyl can also be obtained by the decomposition of some carbon monoxide addition products of univalent nickel,[2] e.g. $NiCN(CO)_x$ and $NiSH(CO)_x$. To overcome the slowness of the reaction between the metals and carbon monoxide, the temperature has to be raised to several hundred degrees in order to obtain a yield of some of these compounds. Only nickel and iron carbonyls are formed at atmospheric pressure; for the preparation of all the others a very considerable increase of pressure is necessary: e.g. for $Ru(CO)_5$ at 180 atm. pressure at 180° and for $Mo(CO)_6$ at 200 atm. at 200°. Recently Hieber and his co-workers[3] have used with success a rotating autoclave, capable of withstanding pressures up to 300 atmospheres, and lined with Cu or Ag. A typical reaction is

$$2CoS + 8CO + 4Cu = [Co(CO)_4]_2 + 2Cu_2S,$$
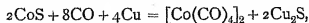
the copper being obtained from the autoclave lining. In the presence

[1] Mond and co-workers, Chem. News, 1890, 62, 97; 1891, 64, 295; Z. anorg. Chem., 1910, 68, 207; Hieber, Mühlbauer and Ehmann, Ber., 1932, 65 [B], 1090.
[2] Manchot and Gall, Ber., 1926, 59, 1060; 1929, , 678.
[3] Hieber, Schulten and Marin, Z. anorg. Chem., 1939, 240, 261; 243, 145; see also Welch, Ann. Rep. Chem. Soc., 1941, 37, 71.

of water, carbonyl hydrides may be formed (see below). Halides or complex halides, e.g. K_2IrCl_6 may be used in place of sulphides:

$$2CoI_2 + 4Cu + 8CO = [Co(CO)_4]_2 + 4CuI,$$
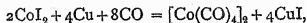
in which particular reaction $Co(CO)I_2$ may be formed as an intermediate product. The high-pressure method has also been applied to the preparation of $Zn(Co(CO)_4)_2$, $Cd(Co(CO)_4)_2$, $[Ir(CO)_3]_n$, $[Ir(CO)_4]_3$ and $HIr(CO)_4$. $[Co(CO)_3]_4$ is obtained by heating the tetracarbonyl to $52°$.

$Cr(CO)_6$ and $W(CO)_6$ are obtained by heating $CrCl_3$ or WCl_6 with CO and phenyl magnesium bromide. The extent of the polymerisation of the polymetallic types is found by molecular weight determinations. The preparation and decomposition of these compounds is a reversible procedure. The compounds in the preceding table which are richest in carbon monoxide are nearly always formed first, and from these the lower ones may be prepared by thermal decomposition. For the decomposition and technical importance of nickel carbonyl for the production of nickel, cf. p. 201.

The carbonyls of the metals may be subdivided into two groups: the monometallic carbonyls are volatile and readily soluble in indifferent organic solvents, while the bi- and poly-metallic carbonyls are difficult to volatilise and are insoluble or very slightly soluble in such liquids.

All carbonyls split up into the metal and carbon monoxide when sufficiently heated. They serve as reducing agents, and when mixed in the form of vapour with air may even explode violently. They are not attacked by acids, nor dissolved by water, although they are soluble in many organic solvents. The more electropositive metals, like magnesium, cannot give rise to such carbonyl compounds, since they are oxidised by carbon monoxide on heating. For the reaction of NO with the carbonyls cf. p. 682.

The structure of carbon monoxide itself is of significance in arriving at the structures of the carbonyls; evidence from the parachor, heat of formation, dipole moment, the force constant and the interatomic distance lead to the formula[1] $:\overset{..}{\underset{..}{C}} :: \overset{+}{\underset{..}{O}}:$, i.e. $C \leqq O$. Pauling has put forward evidence in favour of resonance between $\overset{+}{\underset{..}{C}} :: \overset{..}{\underset{..}{O}}:$ and $:\overset{..}{\underset{..}{C}} :: \overset{+}{\underset{..}{O}}:$, with a preponderance towards the latter. Formation of monometallic carbonyls probably takes place through the sharing of the "lone pair" of carbon electrons with the metal, $M \leftarrow C \equiv \overset{+}{O}$, i.e. $M—C \equiv \overset{+}{O}$, and the inert gas shells are thereby attained by the metals, which do not contribute any electrons themselves. Thus in the stable

[1] Hammick, New, Sidgwick and Sutton, J. Chem. Soc., 1930, 1876; see also Sidgwick, "Covalent Link in Chemistry," 1933, p. 187; Blanchard, Chem. Reviews, 1937, 3.

monometallic carbonyls the total number of extranuclear electrons of the metals become equal to those of the inert gases:

Carbonyl.	Extranuclear electrons of metal atom.	Electrons contributed by CO group.	Sum.
$Cr(CO)_6$	24	2×6	36
$Mo(CO)_6$	42	2×6	54
$W(CO)_6$	74	2×6	86
$Fe(CO)_5$	26	2×5	36
$Ru(CO)_5$	44	2×5	54
$Ni(CO)_4$	28	2×4	36
$Os(CO)_5$	76	2×5	86

In a sense, the metals are exhibiting zero valency in these compounds, and are showing a resemblance to the inert gases. The same effect is probably present in the polymetallic carbonyls, and indicates also why monometallic carbonyls are not formed by elements of odd atomic number, e.g. Co, atomic number 27.

Sidgwick and Bailey[1] pointed out that the general relation $G - \frac{xm + 2y}{x} = x - 1$ holds for all known carbonyls $M_x(CO)_y$ where m is the atomic number of M and G that of the next inert gas. In the polymetallic carbonyls, polymerisation must be produced by co-ordination both of carbon and of oxygen to give $\overline{M}$--$\overset{+}{C}$≡$\overset{+}{O}$—$\overline{M}$ bonds. It is unlikely that the metallic atoms are directly linked, for such bonds are practically unknown, except in mercury compounds. If this bonding results in each metallic atom having the number of electrons in the inert gas shell, the number of oxygen co-ordination links, from the equation, equals 1 when $x=2$, 3 when $x=3$ and 6 when $x=4$. This suggests that each metallic atom is linked through carbon monoxide to all the others, and leads to linear, triangular and tetrahedral forms as shown below; the lines indicate only the possible directions of the bonds.
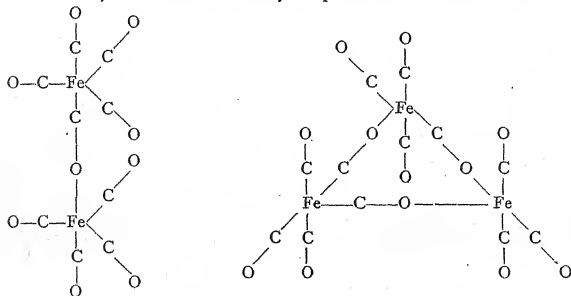
[1] Proc. Roy. Soc., 1934 [A] 144, 521.
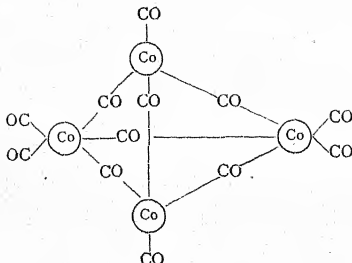
The extranuclear shell of the next inert gas is not reached by each cobalt atom in $[Co(CO)_3]_4$, but is an average effect in the structure

shown.   Likewise in
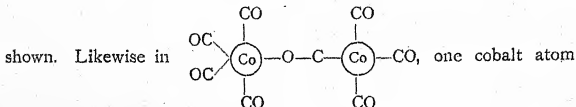
has an effective atomic number of 37 and the other of 35.   The spatial arrangements of the groupings in these molecules have not been fully elucidated.   The results of X-ray analysis[1] are not without ambiguity. In $Fe_2(CO)_9$ the data agree with the long linear vertical axis shown; the other groupings, each of $3CO$, are possibly inclined at 90° to the vertical CO groups and at 60° to each other. $Ni(CO)_4$ is almost certainly tetrahedral,[2] as determined by electron diffraction measurements, and the Ni—C—O bonds are linear.   The dipole moment (0.3×10^{-18} e.s.u.) also agrees with the symmetrical tetrahedral structure.[3]

The reactions of iron carbonyl with ethylenediamine give first an additive compound $Fe(CO)_5$en, followed by the elimination of CO and formation of $Fe_2en_2(CO)_5$, which is crystalline and stable towards air and is related to $Fe_2(CO)_9$, one replacing $2CO$ groups.   With dilute weak acids:

$$Fe(CO)_5Fe\ en_2 + 6HX \longrightarrow FeX_2 + Fe(CO)_5 + 2en(HX)_2 + H_2.$$
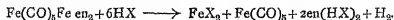
The red compound $Fe(CO)_5Fe(en)$ or $Fe(CO)_4\ Fe(CO)en$, which is very unstable when moist, can be extracted with ether.   Pyridine gives a complex reaction with iron carbonyl and hydrazine a dark red syrup, with evolution of 4 mols. of CO per mol. of hydrazine.[4]   The following compounds and others have also been prepared :

$Fe(CO)_3(NH_3)_2,\quad Ni(CO)_2(o\text{-phenanthroline}),\quad Cr(CO)_3(py)_3,\quad Mo_2(CO)_6en_3,\quad W(CO)_4py_2.$
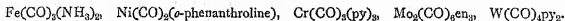
Nickel carbonyl is very sensitive to the oxygen of the air in the presence

[1] Brill, Z. Kristallogr., 1927, 65, 89 ; 1931, 77, 36.
[2] Brockway and Cross, J. Chem. Physics, 1935, 3, 821.
[3] Sutton, New and Bentley, J. Chem. Soc., 1933, 652.
[4] Hieber and Sonnekalb, Ber., 1928-30, 61-63.

of alkali, and is oxidised with formation of CO_2 and NiO. Iron carbonyl is still more active, as it removes the oxygen from water when alkali is present, and hydrogen is set free. With ammonia, ammonium carbamate is formed: $CO + 2NH_3 + H_2O \longrightarrow NH_2CONH_4 + H_2$; with barium hydroxide, the carbonate is precipitated. The hydrogen is not liberated as such but forms iron carbonyl hydride, $Fe(CO)_4H_2$, a volatile yellow liquid, m.p. $-68°$:

$$Fe(CO)_5 + 2OH' \longrightarrow Fe(CO)_4H_2 + CO_3''.$$
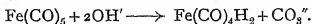
The aqueous solution of this curious compound is yellowish, and although it can be boiled without decomposition in the complete absence of air, it is so sensitive to oxygen that it can be used in vat dyeing; it reduces methylene blue quantitatively, and this reaction can be used to estimate the combined hydrogen present. Active oxidising agents dehydrogenate the compound, e.g. MnO_2 gives $[Fe(CO)_4]_3$ which can thus be made in this way. Acids are stated to cause rapid decomposition $2Fe(CO)_4H_2 \longrightarrow Fe(CO)_5 + Fe(CO)_3 + H_2$ so that the lower ferrocarbonyls can be prepared in this way. Further, with alkali, $2Fe(CO)_4 \longrightarrow Fe(CO)_5 + Fe(CO)_3$ and the latter yields $Fe(CO)_2$ together with higher carbonyls.[1]

Iron carbonyl hydride is an acid, and forms salts,[2] of which the following are examples:

$$NaH[Fe(CO)_4], \quad Hg[Fe(CO)_4], \quad Hg_2Cl_2[Fe(CO)_4], \quad Cd[Fe(CO)_4],$$
$$[Ni(NH_3)_6]H_2[Fe(CO_4)]_2.$$
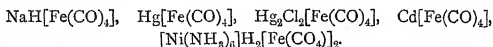
The hydrogen is not attached direct to the metal but through the CO group and the formulation may be $Fe(CO)_3(COH)_2$ or for the cobalt compound, $Co(CO)_3COH$.

Cobalt carbonyl $Co_2(CO)_8$ is another carbonyl giving similar reactions, but the formation of $H[Co(CO)_4]$ is indicated only by the preparation of salts of the above types. In the acid $\overset{+}{H}[Co(CO)_4]^-$ cobalt has a shell of 36 electrons, and has thus attained the inert gas form ; it appears, however, to be unstable. $H_2Ru(CO)_4$ and $HIr(CO)_4$ may also exist.

The halogen derivatives $Fe(CO)_4X_2$ where X is Cl, Br or I can be obtained, also $Re(CO)_5X$.

The metallic carbonyls are co-ordination compounds from which CO can be split off unchanged, as contrasted with other addition compounds, in which the bivalent carbon becomes quadrivalent. To the latter class belong the addition compound with oxygen, CO_2 —the combustion of CO takes place with a blue flame ; the addition compound with sulphur, carbon oxysulphide, COS (p. 846), and

[1] Hieber and Leutert, Z. anorg. Chem., 1932, **204**, 145.

[2] Feigl and Krumholz, Monatsh., 1932, **59**, 314 ; Hock and Stuhlmann, Chem. Ztg., 1931, **55**, 874.

finally that with chlorine, gaseous phosgene, $COCl_2$, the chloride of carbonic acid, which is best formed by the action of sunlight (p. 811). Bromine and iodine do not combine with carbon monoxide. On the other hand, strong bases combine readily with it if the delay in the reaction is reduced by raising the temperature, and, where possible, by increasing the pressure. In this way potassium hydroxide reacts in solution or in the solid condition, when treated with carbon monoxide under 3-4 atm. pressure, with a velocity which falls very little short of the rate of reaction of CO_2 with KOH. Potassium formate is produced: $CO + H . OK \longrightarrow H . CO . OK$, and calcium formate may also be prepared very easily in a similar way. Potassium formate is also produced by the action of carbon monoxide on potassium hydride: $2CO + KH \longrightarrow H . COOK + C$, and a still more complicated organic compound, potassium hexahydroxybenzene, $(COK)_6$, is formed as a direct addition product of carbon monoxide and metallic potassium when the two substances are brought together at 80°. This very explosive compound is formed by the simultaneous linkage of the carbon atoms of several CO molecules with each other. It is also easily formed if the preparation of potassium is carried out by the reduction of one of its compounds by means of carbon (p. 189). For details of this compound text-books of organic chemistry should be consulted. It is notable that an analogous compound of sodium is not formed, perhaps because it is much more easily decomposed. On the other hand, the sodium compound of another group of alkali metal carbonyls is known, KCO, NaCO, etc., which are likewise explosive, but are distinguished by their bright colour; the lithium and rubidium compounds are, however, white. They are formed when carbon monoxide is passed into a solution of the alkali metals in liquid ammonia at $-50°$. They gradually decompose at ordinary temperatures[1]: $4NaCO \longrightarrow Na_2CO_3 + Na_2O + 3C$. They are probably of the type M^+CO^- (compare p. 623).

With hydrogen carbon monoxide forms methane $CO + 3H_2 \longrightarrow CH_4 + H_2O$ on heating, or at lower temperatures if the mixed gases are passed over finely divided nickel or cobalt.

Preparation of Carbon Dioxide.—Carbon dioxide is formed in the equilibrium between carbon and oxygen, as discussed on p. 782 *et seq.* It may, however, be obtained by the action of other oxidising agents on carbon. Fuming nitric acid reacts with powdered wood charcoal at ordinary temperatures with emission of sparks and evolution of nitrous gases, and concentrated sulphuric acid is reduced on heating with wood charcoal with the formation of the oxides of carbon and sulphur: $2H_2SO_4 + C \longrightarrow CO_2 + 2SO_2 + 2H_2O$. If the substances containing oxygen are solid at the ordinary

[1] Joannis, *Compt. rend.*, 1893, 116, 1520.

temperature they must be heated to the melting point to bring about intimate contact with the carbon. The best known of these reactions are those of molten nitrates, chlorates and iodates with carbon, which are very violent and may in some cases take place with explosion. Manganese dioxide also gives carbon dioxide on heating with carbon to red heat.

Carbon dioxide can also be obtained from compounds in which it is already present in the combined condition, *e.g.* from carbonates. If carbonates are acted on with acids, carbonic acid, H_2CO_3, is first formed, which splits up to a great extent into its anhydride and water: $H_2CO_3 \longrightarrow H_2O + CO_2$, and since the CO_2 is only very slightly soluble in water, and still less in acids, it escapes, as its solubility product is quickly exceeded. More must then be formed in solution to maintain the equilibrium with the undecomposed carbonic acid, and this process continues until the carbonate is completely decomposed. For this reason the CO_2 can be displaced from carbonates by acids which are even weaker than carbonic acid, *e.g.* with acetic acid. Very weak acids like HCN give so little H_2CO_3 that the CO_2 caused by this decomposition can remain in solution, and in this way the reaction proceeds no further. Similarly, concentrated anhydrous acids, *e.g.* conc. sulphuric acid, give no carbon dioxide with carbonates, since they lack the necessary hydrogen ions for the formation of carbonic acid. At higher temperatures acids much weaker than carbonic acid also decompose carbonates, especially in the fused state, since the double decompositions can be completed with the help of their anhydrides. Thus the carbonic acid can be completely removed from alkali carbonates by fusion with silica, although the silicic acid is considerably weaker than the carbonic acid. In the melt there is a condition of equilibrium, *e.g.*:

$$Na_2CO_3 + SiO_2 \rightleftharpoons Na_2SiO_3 + CO_2,$$
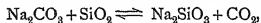
and although this equilibrium certainly lies more on the left side of the equation the transposition is almost quantitatively complete, because the very small quantities of CO_2 which are formed, being completely insoluble in the melt, escape in the gaseous condition and more must be formed to maintain equilibrium. This reaction is commonly used for the opening up of silicates.

On heating carbonates a condition of equilibrium is normally attained: $MCO_3 \rightleftharpoons MO + CO_2$, and if the CO_2 can escape it is driven off completely, if its dissociation pressure at the temperature at which the decomposition is carried out is higher than the pressure of the carbon dioxide in the air or in the gases from the flame by which the heating is completed. This is not the case if an alkali carbonate is heated on the ordinary Bunsen flame; here no temperatures are attainable at which the CO_2 pressure of the

carbonate is greater than the CO_2 concentration of the surrounding atmosphere. On this account the decomposition of the alkali carbonates is very slight, and so far as it happens at all is partly to be attributed to hydrolysis by atmospheric moisture. But the carbonates of the alkaline earths have higher dissociation pressures, and can therefore be converted into oxides; calcium carbonate is most readily decomposed. The dissociation of magnesium carbonate might be expected to be simple as well, but it is not directly decomposed to magnesium oxide, as the oxide and carbonate give a series of solid solutions in each other, in which the CO_2 pressure becomes smaller the richer they are in oxide: e.g. pure $MgCO_3$ has a CO_2 pressure of 1 atm. at a temperature of about 230°, but when the composition has been altered to $9MgO . 8CO_2$, $7MgO . 6CO_2$, $5MgO . 4CO_2$ by driving off the carbonic acid, the dissociation temperature rises to 295°, 340° and 405° respectively. The carbonates of lanthanum, neodymium and praseodymium give off their CO_2 in two well-defined stages: two-thirds is set free at 550°, the remaining compound, $M_2O_3CO_2$, being very stable but dissociating sharply at 800° for Nd, 815° for Pr and 905° for La.

The carbonates may be regarded as complex anionic compounds of the metallic oxide with carbon dioxide of the type $M[O(CO_2)]$, and in accordance with the general rule for all such anionic complexes, the carbonates of comparable metals are the more stable the greater the volume of the cation. Thus potassium carbonate is more stable to heat than sodium carbonate, and barium carbonate is more stable than calcium carbonate. A decomposition pressure of 1 atm. of CO_2 is attained at approximately the following temperatures:

Ag_2CO_3	$PbCO_3$	$MnCO_3$	$FeCO_3$	Li_2CO_3
275°	347°	327°	405°	1270°.
$MgCO_3$	$CaCO_3$	$SrCO_3$	$BaCO_3$	
230°	817°	1258°	1297°	

In the series of alkali carbonates there is an exception to the above rule, for the dissociation pressure of potassium carbonate is least, and it then increases in passing to caesium carbonate. At a temperature of 1200° the alkali carbonates show the following dissociation pressures:

	Li_2CO_3	Na_2CO_3	K_2CO_3	Rb_2CO_3	Cs_2CO_3
ca.	300	41	27	60	95 mm. of mercury.

At 800° potassium carbonate has a dissociation pressure of less than 1 mm. of mercury.

Adequate confirmation of these temperatures is difficult, however, because only few of the equilibria $MCO_3 \rightleftharpoons MO + CO_2$ are reversible in practice. It is probable that the metallic oxide first formed soon changes into a less reactive form which has very little or no further

ability to take up carbon dioxide. There are thus in the cyclic process three reactions:

I. $MCO_3 \longrightarrow MO_a + CO_2$.   II. $MO_a \longrightarrow MO_b$.   III. $MO_b + CO_2 \longrightarrow MCO_3$.
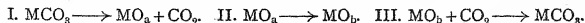
Reaction III. is not the mere reverse of reaction I. The conversion $MO_a \rightarrow MO_b$ may be only a superficial change, but it may also be an internal change in the orientation of the MO molecule. The addition of CO_2 to MO_b is usually not at all complete, or else it is extraordinarily slow. Ignited copper oxide takes up no carbon dioxide, and the considerable quantities taken up by lead oxide vary with the method and degree of heating and the more or less complete conversion into MO_b. Lime can be completely reconverted to the carbonate when it has been burnt at a low temperature, and on stronger ignition it is dead-burnt and no longer combines with water, or only with difficulty.

Carbon dioxide is prepared commercially by heating the carbonates of calcium and of magnesium. Bicarbonates give off the gas at still lower temperatures, thus:

$$2NaHCO_3 \longrightarrow Na_2CO_3 + H_2O + CO_2.$$
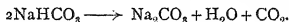
A dissociation pressure ($CO_2 + H_2O$) equal to 1 atm. is given by :[1]

	NaHCO$_3$	KHCO$_3$	RbHCO$_3$	CsHCO$_3$
At . .	102°	157°	164·5°	175·5°,

so that even on boiling their aqueous solutions the gas is copiously evolved, and the CO_2 pressure in the solution always remains very low. Solutions of calcium bicarbonate also decompose completely on heating, with deposition of carbonate (fur of kettles; boiler scale).

Carbon dioxide is also obtained from numerous organic compounds, *e.g.* it is abundantly produced in many processes of fermentation.

Structure of Carbon Dioxide.—Carbon dioxide is a non-polar compound exhibiting typical covalency. The crystal structure of CO_2 as determined by the X-ray method shows that the two oxygen atoms do in fact lie on opposite sides of the carbon atom, that is, the molecule is linear. This linear arrangement also agrees with the observed zero dipole moment of carbon dioxide; if the valency directions were inclined at less than 180°, the molecule would have a measurable moment. The bond distances in carbon dioxide were found by Wierl[2] to be 1·13 Å, which is much lower than the expected value of 1·28 Å (*cf.* p. 23). This indicates that the carbon dioxide molecule is a mesomeride (see p. 348) between the double-bond type $O{=}C{=}O$ and excited triple bond types $\overset{+}{O}{\equiv}C{-}\overset{-}{O}$ and $\overset{-}{O}{-}C{\equiv}\overset{+}{O}$. If the molecule approaches closely towards these triple bond forms

[1] R. M. Caven and H. J. S. Sand, *J. Chem. Soc.*, 1911, 99, 1359 ; 1914, 105, 2752.
[2] *Ann. Physik.*, 1932, 13, 453.

the observed shortening of the bond distances would be satisfactorily explained.

Properties of Carbon Dioxide.—Carbon dioxide is a colourless, odourless gas. Since it forms carbonic acid with the moisture of the tongue, and hydrogen ions are produced, it has a sour taste. Carbon dioxide can be liquefied only under pressure—cold alone converts it directly to the solid condition; reversibly, solid CO_2 gasifies without first melting. At $-79°$ its vapour pressure is equal to one atmosphere, while its melting point is $-56.4°$, a temperature at which solid CO_2 can exist only under a pressure of 5.1 atmospheres. If, therefore, liquid carbon dioxide is allowed to escape from a cylinder into the air, it solidifies immediately and forms a loose white snow-like mass, because the pressure is reduced to one atmosphere. It may also be obtained in large cubic crystals as clear as water by cooling the liquid form. This solid gives a pressure of 35 atm. at 0°, and 56 atm. at 20°; the critical temperature is about $31.5°$, the critical pressure being 75 atm., and it is a specially useful material for the study of critical phenomena.

The low temperature of solid carbon dioxide, which is very easily obtained, makes it a useful cooling medium. The carbon dioxide, however, does not cling to the sides of the vessel, and an envelope of carbon dioxide gas is formed round the object to be cooled; such a layer of gas conducts heat very badly and diminishes the rate of cooling. For this reason solid carbon dioxide is best mixed with a liquid which facilitates the exchange of heat (ether, acetone). The temperature is not substantially lowered in this way, as the eutectic temperature of the CO_2—ether solution lies only a little below the distillation temperature of carbon dioxide, and the object of the mixture is chiefly the promotion of mechanical contact. Liquid carbon dioxide is easily soluble in alcohols as well as in ether, and forms compounds with them; the compounds with alcohols contain one molecule of each of the components, and have higher melting points than the alcohols themselves. Carbon dioxide also forms a hydrate with water, to which the formula $CO_2.6H_2O$ has been given but this compound can be observed only under pressure, e.g. under 6.5 atm. at $6°$. The solutions of carbon dioxide which are obtainable at room temperatures do not contain this hydrate. Alcohol dissolves 3 vols. of the gas at 20°, and water still less, viz.:

	0°	15°	30°	60°
Vols. CO_2	1.71	1.02	0.66	0.36 per vol. H_2O.

The CO_2 content of beer may be considerably greater owing to the fact that the colloidal substances in it can adsorb the gas, and super-saturated solutions of carbon dioxide of considerable concentration can

be made, as may be seen in all mineral waters. The fewer the solid particles contained in these waters (serving as nuclei for the gas bubbles) the longer does the supersaturation remain unchanged. For that reason drinks containing CO_2 which have been bottled for a long time froth less than fresh samples, since the solids originally in suspension cling to the surface of the glass when the liquids are poured out.

Liquid carbon dioxide is itself a poor solvent for other substances. Iodine, bromine, phosphorus, boric acid and a few other inorganic substances are soluble in it, but no salts (distinction from liquid NH_3 and SO_2). But it is very remarkable that its vapour has a considerable solvent action on some substances (iodine, camphor), which are miscible with it above the critical temperature where no liquid carbon dioxide exists.

The aqueous solution of carbon dioxide is only a very weak acid, *e.g.* litmus paper is not coloured red, but wine colour. But it would be illusory to decide upon the actual strength of the carbonic acid on such grounds or even from conductivity measurements. It is not possible to find out how much of the carbonic acid is present as H_2CO_3 in the solution, and how much consists of unhydrated CO_2. In fact, the weakness of carbonic acid on account of its appreciable decomposition into water and CO_2 is deceptive, and probably it is about twice as strong as formic acid. What had previously been found as the dissociation constant of carbonic acid was not I., but II.

$$\text{I.} \quad \frac{H^{\cdot} \times HCO_3{'}}{H_2CO_3} = K. \qquad\qquad \text{II.} \quad \frac{H^{\cdot} \times HCO_3{'}}{H_2CO_3 + CO_2} = K'.$$

The true value of its acidity was first determined by Thiel and Strohecker [1] on the basis of the data of McBain,[2] who suggested that the reactions between CO_2 and bases do not occur instantaneously, but proceed gradually. Dilute solutions of bases tinted with phenolphthalein are decolorised only after a measurable period of time by the addition of a solution of carbonic acid, although for a small portion of the base the decoloration is immediate. The carbonic acid corresponds only to this portion, and all the rest of the CO_2 in solution is transformed gradually into H_2CO_3, or to put it more accurately, it is the reaction $CO_2 + OH' \longrightarrow HCO_3{'}$ which proceeds at a measurable rate.

Although carbon dioxide does not form addition compounds with metals as readily as the monoxide, a 17 per cent. yield of potassium oxalate is obtained when it acts on potassium at 230° to 240°.

CARBONATES

Carbonates owe many of their properties to the weakness of the acid. They are strongly hydrolysed in solution in water, and even

[1] *Ber.*, 1914, 47, 945, 1061.   [2] *J. Chem. Soc.*, 1912, 101, 814.

those of the alkali metals are largely decomposed with formation of the alkali hydroxides. A $0.19N$ Na_2CO_3 solution is hydrolysed at room temperature to the extent of 2·12 per cent., and a $0.03N$, 7·1 per cent. For this reason solutions of these carbonates have a strongly alkaline reaction. The carbonic acid set free on hydrolysis does not escape when the base is strong, but forms the bicarbonate :

$$Na_2CO_3 + H_2O \rightleftharpoons NaOH + NaHCO_3.$$
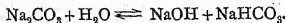
The solution of the pure bicarbonate, however, still contains free OH' ions, and is therefore alkaline in reaction, but only slightly so, and if such a solution coloured red by phenolphthalein is cooled to $0°$ the hydrolysis is repressed to such an extent that the red colour vanishes. The hydrolysis increases on heating, and as the CO_2 split off is not chemically combined, it escapes. Even a Na_2CO_3 solution begins to lose carbon dioxide on boiling, and more than 13 per cent. may come off in twenty-four hours, if the access of gases from the flame is prevented. The escape of the gas into the air is limited by the pressure of the carbon dioxide in the atmosphere, and if the solution is exposed the sodium hydroxide formed takes up CO_2. When a gas flame is used and the boiling carried out in an open vessel the carbon dioxide formed is sufficient to nullify the escape of this gas from the solution.

This tendency to hydrolysis causes the carbonates of weakly basic metals to be unstable. Salts of tervalent iron, chromium and aluminium do not give a carbonate on treatment with sodium carbonate; almost pure hydroxides are formed, containing very small quantities of carbon dioxide, possibly the result of adsorption. Other metals of high valency (thorium, zirconium, titanium) behave similarly, and give only precipitates of very basic salts. The presence of sodium hydroxide in sodium carbonate solutions causes the metals present to form hydroxides on precipitation whenever the hydroxides are less soluble than the carbonates. The difference in solubility is not very great as a rule, so that mixtures of hydroxide and carbonate separate which are frequently regarded as basic carbonates. Bismuth salts form only basic carbonates, $(BiO)_2CO_3$, in keeping with the general tendency of bismuth salts to hydrolyse, and similarly the mercuric salts give basic carbonates—mostly the brown $3HgO . CO_2$—even on precipitation with bicarbonate. Copper forms only exceptionally basic salts, of which the main types are the green malachite form, $CuO, CuCO_3$, aq., and the blue azurite form $CuO, 2CuCO_3, H_2O$ (copper lapis lazuli). Both types occur in nature and can also be obtained artificially ; normal copper carbonate, $CuCO_3$, on the other hand, does not appear to exist. Patinas, formed when copper is exposed to the atmosphere, are often considered to be basic copper carbonates, but Vernon and Whitby[1] have shown that these

[1] *J. Inst. Metals*, 1930, 44, 389.

materials are basic sulphates, identical in composition with the mineral

brochantite, $\left[Cu \left\langle \begin{matrix} H \\ O \\ O \\ H \end{matrix} \right\rangle Cu \right)_3 \right] SO_4$; in districts near the sea,
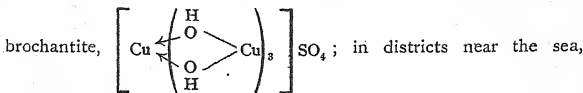
sulphate is partially replaced by chloride.

The carbonates of magnesium, zinc, nickel and cobalt, which form white, green and pink precipitates respectively, almost always separate in the basic form. The magnesium compound, "magnesia alba," a white amorphous powder, usually has the composition $Mg(OH)_2$, $3MgCO_3$, $3H_2O$. All these basic carbonates may be converted into the normal carbonates by allowing them to stand for a considerable time, or better by heating, in a solution of an alkali bicarbonate. The normal salts are also formed if the chlorides are heated with marble in a closed tube at 180°. With copper salts, however, malachite only is obtained in this way, and no normal salt. It is remarkable that the most strongly basic of the rare earths give only approximately neutral carbonates when precipitated with sodium carbonate in the cold and highly basic ones when the solution is hot. Normal carbonates are obtained only when sodium bicarbonate saturated with carbon dioxide is used for precipitation, but the hydrolysis on boiling does not exceed the stage represented by $M(OH)CO_3$.

In contrast to this, the normal carbonates are obtained by precipitation with sodium carbonate solution, provided they are considerably less soluble than the hydroxides. They frequently appear in the crystalline form. This occurs with the alkaline earths (except magnesium), thallium, silver, lead, manganese and cadmium. Basic carbonates are not formed by these metals, but basic lead carbonate can be obtained by a different process. Normal lead carbonate, once prepared, does not hydrolyse even at 100° if the escape of the carbon dioxide is prevented; but the basic carbonate (white lead) can be formed by the gradual addition of carbonic acid to a lead salt, e.g. by exposing metallic lead to carbonic acid and the vapours of a slightly corrosive acid. This was originally done by keeping the lead in chambers in which acetic fermentation was carried out, or in which it was left in contact with vinegar in the presence of atmospheric air. At present an electrolytic process is mainly used for the preparation of white lead, but the basic carbonate may be formed in larger crystals, and its covering power thus diminished. White lead corresponds approximately to the composition $2PbCO_3$, $Pb(OH)_2$.

Solubility and Hydrated Forms.—All the carbonates, with the exception of those of the alkalis and of univalent thallium, which also has a soluble hydroxide, are very insoluble in water. Even lithium carbonate dissolves only very slightly: 0.154 g. at 0°, 0.073 g.

at 100° in 100 c.c. water. Here again the lithium salt shows its approach to the properties of the alkaline earth salts, as also in the diminution of the solubility with rise in temperature. This property is found throughout the alkaline earth carbonates, e.g. of magnesium carbonate at 15°, 0·0095 mole dissolves per litre, and 0·0071 per litre at 33°. Barium carbonate is more soluble than calcium carbonate, a fact which renders possible the analytical separation of the alkaline earths by the sulphate-carbonate mixture. The solubility of the carbonates of the heavy metals is extremely low, e.g. that of the bright yellow silver carbonate is only $1·14 \times 10^{-4}$ g. mols./litre.

The solubility of these carbonates can, however, be very considerably increased by passing in carbon dioxide. By analogy with the alkali carbonates, in which the acid carbonates are formed by this process, it might be expected that the other carbonates are dissolved owing to the formation of acid salts, although hitherto none of these has been obtained in the solid condition. In practice, the carbon dioxide splits off again, and the normal carbonate separates instead; this gives a method of converting basic to normal carbonates. The solubility naturally increases with increasing pressure of carbon dioxide, as is shown in the following table for barium carbonate:

CO_2 press. in atm.	0·00	0·139	0·142	0·982
$BaCO_3$ mg./litre (18°)	24	233	916	1857

The behaviour of calcium carbonate is similar. Here the solubility at room temperature is:

CO_2 press. in atm.	0·00	0·139	0·142	0·984
$CaCO_3$ mg./litre	13	223	533	1086

The solubility of lead carbonate in water is raised almost ten times by the addition of 0·01 mol. of carbon dioxide.

It may be assumed, perhaps, that the solubility of these carbonates in carbonic acid does not depend on the formation of simple primary salts, but that complex forms take part as well. The so-called acid salts would then be formulated as carbonato-acids, $H_2[M(CO_3)_2]$. Many precipitated carbonates dissolve again if an excess of the alkali carbonate used as a precipitating agent is added (Th, Ti, Ag), and from these solutions double salts may be obtained by crystallisation, e.g. K_2CO_3, Ag_2CO_3; $M_6[Th(CO_3)_5]$ where M can be Na, K, NH_4 or Tl; $Na_6[Ce(CO_3)_5]$; other carbonates (e.g. of Ca, Mg, Cu, Co, Ni and the rare earths) give these double salts, without going into solution, when they are digested for a long time with concentrated alkali carbonate. The double carbonates of the second group are also very difficultly soluble, but are more soluble than the simple carbonates. These double salts decompose if they are acted upon by pure water, the alkali carbonates being split off. Their composition corresponds approxi-

mately to the formula $M^I_2CO_3$, $M^{II}CO_3$, $4H_2O$. Calcium magnesium carbonate, $CaMg(CO_3)_2$ (dolomite) is closely related to these double salts.

If a carbonate exists in several modifications its solubility is naturally dependent upon its form. Such varied forms are best known in calcium carbonate. On precipitation by soluble carbonates it is first obtained in an amorphous or crystalline hydrated form, in which it remains as long as large quantities of free hydroxide are left in the solution. It crystallises finally, either in the form of calcspar (calcite) or in that of aragonite, the latter being probably the less stable. The aragonite is more soluble than basic cobalt carbonate, the calcspar less, and it is thus possible to distinguish the two forms even in indifferent crystals. If aragonite is shaken with a solution of a cobalt salt, it becomes covered with a film of cobalt carbonate and is coloured pink, while calcspar does not do this (Meigen's reaction). Carbonates of bivalent metals crystallise in the calcite form when the ionic radius lies between 0·78 and 1·06 Å, and in the aragonite form when it is between 1·06 and 1·43 Å. The radius of the Ca ion being 1·06 Å, the carbonate exists in both forms.

The precipitation of calcium carbonate is a very suitable way of studying the production of " somatoid " forms.[1] Under this heading are brought all lifeless forms which have regular jointing and grouping without actual crystalline form, but having as a rule polyhedral bounding surfaces. When foreign substances are present during crystallisation somatoid forms are obtained which show similarities to the lower forms of living beings or to those of plants; the effects are definitely reproducible. Under the microscope one can imagine one sees growing flowers, leaves, radiolaria, diatoms and other organised forms. The added impurities, which may be either heavy metal salts or dyestuffs, work by the deposition of some colloidal material on the growing nucleus, thus affecting the rate of diffusion of material. The surface tension at the boundary layers and the building of the crystal lattices are also affected, the whole effect giving a modification of style and rate of growth dependent on the kind and concentration of the foreign material present. The influence of a second dissolved substance on the development of crystal faces is well known, as for instance with alum, which normally crystallises in octahedra but can be obtained in cubes by adding urea (cf. p. 238 for a similar effect with sodium chloride).

The normal alkali carbonates and that of thallium are much more easily soluble, and here, in contrast to those mentioned before, the acid carbonates are less soluble and are therefore precipitated from saturated solutions of the normal salts by passing in carbon dioxide.

100 g. of water at 15° dissolve 4 g., and at 100°, 22 g. of thallous carbonate, and the solubility of potassium carbonate in 100 g. water is as follows :

Temp.		0°	50°	100°
Solubility	.	89·4	121	156 g.

Normal ammonium carbonate $(NH_4)_2CO_3$ dissolves almost as easily as the potassium salt, but it is largely decomposed in solution (p. 810).

[1] Kohlschutter, Bobtelsky and Egg, Helv. Chim. Acta, 1925, 8, 457, 697, 703.

The normal carbonates of potassium, rubidium and caesium are deliquescent in air, while the acid salts may be kept unchanged. All acid carbonates are anhydrous.

The solubility of sodium carbonate is of special interest, as this salt occurs in several stages of hydration; the higher hydrates are increasingly soluble with increasing temperature, but the mono-hydrate, which is only stable above 32·96°, dissolves to a lesser extent at higher temperatures; at the transition point of the higher hydrates into the monohydrate a maximum solubility is found.

The diagram (Fig. 60) shows the solubilities and ranges of the better known hydrates of this salt, *i.e.* that containing 10 mols. water (washing
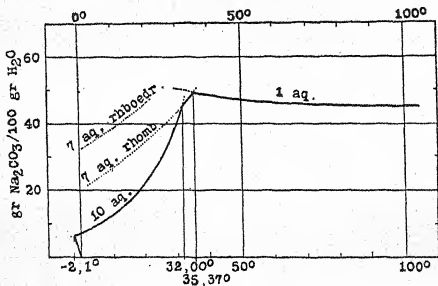
FIG. 60.—Solubility curves of sodium carbonate.

soda), two different heptahydrates and the monohydrate. A eutectic between sodium carbonate and ice, containing 100 parts water to 6·3 parts Na_2CO_3, is formed at −2·1°; the solubility curve of the soda rises from that point, its solubility in 100 g. water amounting to 7·1 g. at 0° and 45·6 g. at 32°. The curve of the monohydrate falls very gently; its solubility at 50° is 47·5, and at 104·75°, 45·1 g. The transition point of the deca- into a hepta-hydrate lies at 32·00°, while that of the hepta- into the mono-hydrate occurs at 35·37°, when that of the deca- into the mono-hydrate has already been completed (at 32·96°). This heptahydrate is unstable for the greater part of its region of existence, and this is even more true of the second hepta-hydrate, as is obvious from the diagram. The latter may be obtained by making use of the fact that the solution of the monohydrate may remain supersaturated for some time on cooling; from this the unstable salt crystallises on suitable treatment and is only converted into the decahydrate later. Besides these hydrates there is still a whole series, *e.g.* a pentahydrate, the conditions of existence of which have not been adequately studied. It can be seen from the above solubility data

that the large clear crystals of washing soda can be melted in their own water of crystallisation. Their dissociation pressure of water vapour is considerable, so that the crystals effloresce in air and do not deliquesce like the potassium salt.

Other carbonates also contain water of crystallisation. Thus potassium carbonate appears with 1, 1·5 and 3 molecules of water, while even the slightly soluble carbonates of magnesium and calcium can be obtained with 3 or 5 mols. and calcium carbonate with 5 or 6 mols. of water. Artificial magnesium carbonate which is dehydrated at low temperature is rehydrated on contact with water or on lying in damp air, and then hardens like plaster of Paris.[1] Natural magnesite ($MgCO_3$) shows this phenomenon very slightly, like naturally occurring anhydrite ($CaSO_4$). The carbonates of the rare earths form octa-hydrates which retain 1 molecule of water of crystallisation when dried at 100.°

Fusibility.—The carbonates fuse with difficulty. For most of them the dissociation temperature, at which they decompose into the oxide of the metal and carbon dioxide (*cf.* p. 797), lies below their melting point, so that they are only fusible under a high pressure of carbon dioxide. Barium carbonate, which has a CO_2 pressure of 1 atm. at 1297°, is still completely unmelted under this pressure at 1380°. On the other hand, calcium carbonate melts under pressure below 1060°, and solidifies on cooling to a mass like marble, composed of calcite crystals. A similar substance is also formed without the use of pressure when this carbonate is heated very rapidly. The carbonates which are easily soluble in water have low melting points, and they are also scarcely decomposed at those temperatures:

	Tl_2CO_3	Li_2CO_3	Na_2CO_3	K_2CO_3
M.pt. . . .	273°	700°	853°	894°.

If it is desired to depress the melting points of the carbonates still further, *e.g.* in the opening up of minerals, a mixture of carbonates is employed. Mixtures of potassium and sodium carbonates melt with little trouble in the Bunsen flame.

Preparation.—Carbonates are formed by double decomposition of a salt of the metal with an alkali carbonate, or with marble on heating to a higher temperature in the presence of water. These modes of formation have already been described above. A third method of preparation is the absorption of carbon dioxide by the oxide or hydroxide of the metal, and carbonates are also obtained on incinerating organic compounds of metals when the temperature of incineration lies below the dissociation temperature. The last method may be used technically for the preparation of potassium carbonate (potashes), which was previously obtained by burning wood and

[1] Engel, *Compt. rend.*, 1899, 129, 598.

lixiviating the wood ashes. Even now a similar method is used for the preparation of pure potassium carbonate by the incineration of the potassium salts of organic acids, which leave behind the potassium carbonate either pure (potassium oxalate) or mixed with carbon (potassium tartrate). In a similar way potassium salts, so important as fertilisers, can be recovered from the beet residues of the sugar factories, but the process is unprofitable and the spent wash from the molasses is used direct as a manure, thus utilising the organic matter as well.

The more easily the hydroxides dissolve in water the more rapidly are the oxides attacked by carbon dioxide. The alkali hydroxides therefore form carbonates immediately, the hydroxides of the alkaline earths somewhat more slowly, but still completely, and the difficultly soluble magnesium hydroxide very slowly indeed. Pure metals which oxidise in air form carbonates at the same time. If the carbonates are also soluble the reaction may take place completely (alkali metals, thallium); if they are insoluble the metal may become enveloped in a film of basic carbonate. If the treatment of the dissolved hydroxide with carbonic acid is completed in the presence of certain protective substances the carbonate is often obtained in the colloidal form. In this way gelatinous barium carbonate may be obtained: if carbon dioxide is passed into a solution of barium hydroxide in methyl alcohol it at first remains completely clear, but later gelatinises suddenly.[1]

The preparation of the alkali carbonates is technically important, and special methods have been worked out, which are not different in principle from the modes of formation above described; these will be studied in some detail in these applications.

Potassium carbonate is obtained from potassium chloride by making use of the fact that a compound of potassium bicarbonate with magnesium carbonate is difficultly soluble. This compound decomposes into its components on heating, and the magnesium carbonate is difficultly, the potassium carbonate easily, soluble. To carry out the preparation $MgCO_3, 3H_2O$ is suspended in a solution of potassium chloride and carbon dioxide is passed in. The double salt $KHCO_3$, $MgCO_3, 4H_2O$ separates, and some of the sodium salts present as impurities remain in solution, so that a separation of the potassium salt from that of sodium is thereby effected. The double salt is either heated with water above 140° or heated dry, when it decomposes with elimination of CO_2, which is used again in the process; the magnesium carbonate remains insoluble when water is added and the potassium carbonate goes into solution (Engel's process).

Sodium carbonate is obtained technically either by saturating caustic soda solution (prepared by the electrolytic process) with carbon

dioxide, or by the decomposition of sodium chloride with ammonium carbonate, when by using an excess of carbonic acid the less soluble sodium bicarbonate separates (Solvay process). This process is effected by dissolving sodium chloride in ammonia and pumping in carbon dioxide; $NaHCO_3$ then separates in the solid state and NH_4Cl remains in solution. The sodium bicarbonate is filtered off and decomposed by heating, the CO_2 being used again in the process. The ammonium chloride which remains in solution is also utilised by heating the solution with lime, when ammonia is liberated and serves for the solution of more common salt, while the only by-product of the process is calcium chloride, for which a specific technical application is still lacking.

Another process for the preparation of soda depends on the decomposition of sodium aluminium fluoride, Na_3AlF_6 (which occurs widely as cryolite), with lime; the decomposition may be carried out either by heating them together to a red heat, or by the wet method: $Na_3AlF_6 + 3CaO \longrightarrow Na_3AlO_3 + 3CaF_2$. The insoluble calcium fluoride and the soluble sodium aluminate are separated by treatment with water. Sodium aluminate solution is hydrolysed to a considerable extent, and if carbon dioxide is passed into it aluminium hydroxide is precipitated, while the soda remains in solution:

$$2Na_3AlO_3 + 3H_2CO_3 \longrightarrow 2Al(OH)_3 + 3Na_2CO_3.$$
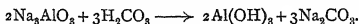
Leblanc's process is the oldest large-scale method for the preparation of soda, but is now almost completely replaced by the above processes. The starting point is sodium sulphate, which is prepared by the decomposition of ordinary salt by concentrated sulphuric acid, when hydrochloric acid appears as a by-product. This sulphate is reduced with coke to the sulphide, which is at the same time converted to sodium carbonate by the addition of calcium carbonate. The two reactions which take place concurrently are:

1. $Na_2SO_4 + 2C \longrightarrow Na_2S + 2CO_2.$
2. $Na_2S + CaCO_3 \longrightarrow CaS + Na_2CO_3.$
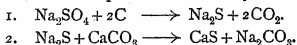
The soda is then obtained by extraction with water, but is always rendered impure by salts containing sulphur, and a good deal of the sodium is lost by remaining in the insoluble portion. The lime always contains silicic acid, which retains the sodium as sodium silicate, as well as iron, which forms an insoluble "iron sodium sulphide" of indefinite composition. This iron sodium sulphide frequently contaminates the soda.

The high price of sulphuric acid makes it desirable to recover it from the calcium sulphide. This is oxidised by allowing it to lie in damp air, and the products formed, which include sulphites, thiosulphates and polythionates, are then decomposed by hydrochloric acid formed in the first part of the process, so that some free sulphur

and some sulphur dioxide are obtained, which are then used as raw materials in the preparation of sulphuric acid.

Ammonium carbonate is obtained synthetically from ammonia and carbonic acid: $2NH_3 + H_2CO_3 \longrightarrow (NH_4)_2CO_3$. The commercial salt never has the composition of the ordinary carbonate but is always a mixture of the bicarbonate, NH_4HCO_3, and ammonium carbamate, $NH_2.CO_2.NH_4$ (*cf.* below). It is converted to the normal salt after digestion for a long time in a strong solution of ammonia. Even then equilibrium exists:

$$2(NH_4)_2CO_3 + aq. \rightleftharpoons NH_4HCO_3 + NH_2CO_2NH_4 + NH_3 + aq.$$
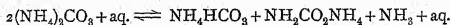
Similarly there is a condition of equilibrium between the bicarbonate and the carbamate:

$$2NH_4HCO_3 \rightleftharpoons NH_2CO_2NH_4 + 2H_2O + CO_2.$$
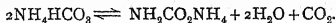
The more water there is present the more of the acid salt is formed. If the addition of ammonia to carbon dioxide is carried out in the absence of water, only the carbamate is formed:

$$C{\Large\langle}\begin{matrix}O\\O\end{matrix} + 2NH_3 \longrightarrow CO{\Large\langle}\begin{matrix}NH_2\\ONH_4.\end{matrix}$$
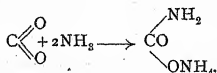
Carbamic acid, NH_2COOH, may thus be regarded as the monamide of carbonic acid.

The ease with which the acid and normal ammonium salts and the carbamate are mutually convertible is due to the fact that all three salts, if they are used in the pure state initially, decompose into CO_2 and NH_3 on heating to the same temperature, viz. 58°. It might be expected that at low temperatures the same tension of ammonia and CO_2 would also be observed, but this is not so, probably because the phenomenon is retarded when water is absent.

Compounds intermediate between the acid and normal alkali carbonates can be obtained. A potassium compound of the formula $K_2CO_3.2KHCO_3$ is known, which is to some extent comparable to the potassium magnesium compound, $KHCO_3.MgCO_3.4H_2O$, mentioned above; sodium sesquicarbonate, $Na_2CO_3.NaHCO_3.2H_2O$, occurs naturally as trona, and is also prepared synthetically.

Finally, the carbonate compounds in which the CO_3 radical is found in a complex cation must be mentioned. The carbonato-tetrammine cobalti-salts are best known, the sulphate $[Co(NH_3)_4CO_3]_2SO_4$ being formed when cobaltous sulphate is oxidised by atmospheric oxygen in the presence of a large excess of ammonium carbonate. It forms cherry-red crystals, easily soluble and very stable. The carbonic acid in them is slowly evolved on treatment with acids.

Thiocarbonates are formed from metallic sulphides and carbon disulphide by a combination similar to that of metallic oxides and carbon dioxide: $BaO + CO_2 \longrightarrow BaCO_3$; $BaS + CS_2 \longrightarrow BaCS_3$. In contrast to free thiocarbonic acid (p. 845), the alkali and alkaline earth salts are very stable, except that they tend to oxidise in solution. The alkali salts are very soluble in water, especially the ammonium salt, $(NH_4)_2CS_3$, which is also obtainable in the crystalline condition, but the thiocarbonates of the alkaline earths are difficultly soluble, and may easily be obtained from alcoholic or aqueous solutions of the components. The salts of the heavy metals are not at all stable; if an attempt is made to obtain them by double decomposition, precipitates are formed which often change colour quickly and sometimes give coloured colloidal compounds. Thus thiocarbonates are reagents for nickel salts, which give a dark brown coloration even at great dilutions. Pure thiocarbonates are bright yellow, but their solutions are red and turn yellow on acidifying like indicators. Similarly, the per-thiocarbonic acids (p. 845) change colour, and when their colourless solutions in organic solvents are shaken with alkali, pale yellow aqueous solutions of the salts are obtained.

Carbonyl chloride, *phosgene*, $COCl_2$, is formed when a mixture of carbon monoxide and chlorine is exposed to light or passed over hot charcoal. It is a colourless gas with a suffocating odour, condensing to a liquid of boiling point 8°. It is hydrolysed by water to carbonic and hydrochloric acids, while with ammonia it forms carbamide (urea) $CO(NH_2)_2$, (see p. 639).

Carbonyl bromide, $COBr_2$, is a liquid stable up to 150°.

Silicon oxychlorides. The following compounds[1] have been isolated from the mixture formed by the action of chlorine and oxygen on red hot silica: $(SiOCl_2)_4$, Si_2OCl_6, $Si_3O_2Cl_8$, $Si_4O_3Cl_{10}$, $Si_5O_4Cl_{12}$, $Si_6O_5Cl_{14}$ and $Si_7O_6Cl_{16}$.

[1] Schumb and Holloway, *J. Amer. Chem. Soc.*, 1941, 63, 480.

OXIDES OF THE ELEMENTS OF THE FOURTH GROUP
(*contd.*): SULPHIDES

Dioxides of Si, Ge, Sn, Pb, Ti, Zr, Th—Hydroxides—Silicates, stannates, etc.—
Siloxanes, etc.—Boron trioxide and boric acid—Hypoborates—Per-acids of the
elements of Group IV and of boron—Sulphur and selenium compounds

Dioxides of Si, Ge, Sn, Pb, Ti, Zr and Th

ALL the elements of the fourth group form dioxides, and these are
the only known oxides of silicon and thorium; but some of these
elements give other oxides also, thus:

Monoxides	.	GeO	SnO	PbO	TiO	...
Trioxides	.	...	...	Pb_2O_3	Ti_2O_3	Zr_2O_3

Other oxides of lead, Pb_2O, Pb_3O_4 (red lead) and Pb_5O_8, have been
obtained. As the lower oxides of this metal behave as basic oxides
they have been described under the metallic oxides on p. 441 *et seq.*

The dioxides of these heavier elements differ from carbon dioxide
in the great affinity they possess for similar molecules, *i.e.* they are
all polymerised and therefore do not exist as gases. They can be
vaporised from the polymerised product only with great expenditure
of energy; they are also difficult to fuse. Polymerisation may occur
in several different ways, *i.e.* they are all polymorphic. Silicon,
germanium, tin, zirconium and titanium dioxides are trimorphic; but
only two forms of thorium dioxide are known, possibly owing to lack of
investigation. The "amorphous" forms are not included here, as they
are, perhaps, only very small crystals. Only one kind of lead dioxide
is known, but that may be due to the fact that this oxide cannot be
subjected to high temperatures. As the most electro-positive of all these
elements, lead forms a greater number of lower oxidation products.

All three different forms of the trimorphic oxides occur in nature.
Silicon dioxide is found as the minerals quartz, tridymite and cristobalite
(chalcedony is small crystals of quartz), titanium dioxide as rutile,
brookite and anatase. In both these oxides the transformation of the
three forms has been closely studied, and it has been found, for instance,
that brookite is formed only between 860° and 1040°, while at higher
temperatures rutile is formed, and, at lower temperatures, anatase.
The three forms are isotrimorphic with those of tin dioxide. In quartz,

tridymite and cristobalite, the three varieties of silicon dioxide, there are also several sub-forms: tridymite changes its optical properties suddenly at 117° and 162°, and cristobalite at 180° and 270°; quartz shows such a marked volume change at about 575° that the crystals often crack above this temperature. At ordinary temperatures the stable form of quartz is obtained, e.g. on heating silica gel with water containing carbonic acid to 250°. Quartz passes into tridymite at 870°, but the reverse change from tridymite into quartz has not been
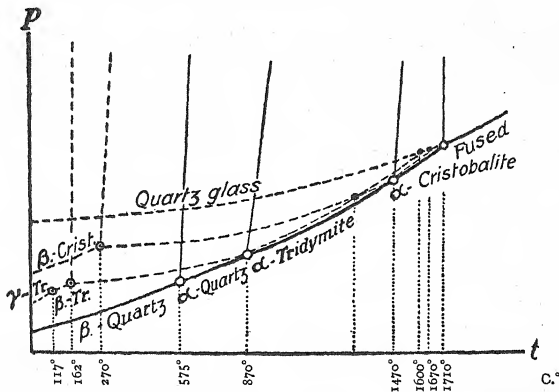
FIG. 61.—Forms of silica.

observed, except in the presence of a suitable solvent. Fused alkali chlorides, borax, or preferably the alkali tungstates or vanadates, act as solvents (also for titanium dioxide, tin dioxide, etc.). The essential difference in the three structures is one of packing. Cristobalite and tridymite consist of a three-dimensional cross-linked network, differing only in the manner of cross-linking, whilst in quartz the arrangement is somewhat distorted, giving rise to Si—O—Si—O—Si spiral chains. (For cristobalite see Fig. 91, p. 887.)

In Fig. 61 the regions of existence of the various forms of silicon dioxide are shown.[1] The transition temperatures are :—

$$\beta\text{-Quartz} \underset{575°}{\rightleftharpoons} \alpha\text{-Quartz} \underset{870°}{\rightleftharpoons} \alpha\text{-Tridymite} \underset{1470°}{\rightleftharpoons} \alpha\text{-Cristobalite} \underset{1710°\pm10°}{\rightleftharpoons} \text{Fused silica}$$

$$\Big\updownarrow 162° \qquad \Big\updownarrow 180°\text{-}270°$$

$$\beta\text{-Tridymite} \qquad \beta\text{-Cristobalite}$$

$$\Big\updownarrow 117°$$

$$\gamma\text{-Tridymite}$$
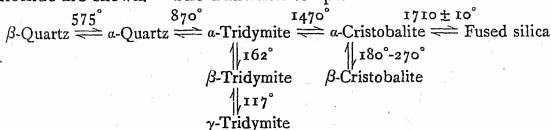
[1] F. Singer, Z. Elektrochem., 1926, 32, 385.

The differences in energy between the single modifications are small, which makes complete mutual conversion difficult. The transition of α- and β-quartz into each other takes place without the collapse of the external crystal form. Quartz is a very beautiful example of enantiotropy. The X-ray diagrams (Figs. 62, 63) give a definite insight into the internal arrangement of the molecules.[1]
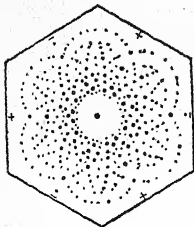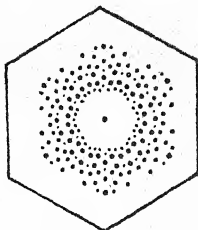
FIG. 62.   FIG. 63.

X-ray diagrams of α- and β-quartz (after F. Rinne).

The melting point of pure quartz is estimated to be 1600°-1670°, that of cristobalite 1710°. In the absence of catalysts SiO_2 shows no definite melting point, because several modifications are present at the same time; it softens gradually as glass does when heated, becomes plastic at 1500°, and can then be fritted to the proper shape for apparatus, which has not yet then the transparency of "quartz glass" (which is completely fused), but appears opaque, and glossy like silk. It may be drawn into thin threads at a somewhat higher temperature. It is a thin liquid at about 1780°. When silicon dioxide vaporises about 1750° (its b.pt. under atmosphere pressure is 2230°) the vapour only partly condenses as tridymite, for a portion forms glassy masses. Fused quartz glass is distinguished by its small volume change with fluctuating temperature, the coefficient of expansion being only $\frac{1}{18}$ of that of glass, so that red-hot quartz vessels may be suddenly cooled by plunging them into water, without fear of cracking owing to internal strains. In titanium and tin dioxides the properties appear to be different. In the former all three modifications melt at 1560°, *i.e.* brookite and anatase are completely transformed into rutile before this temperature is reached; tin dioxide also melts sharply at 1127°.

The dioxides of this group are in general colourless and transparent when pure, with a brilliant lustre, and are harder than glass. Lead dioxide alone is brown and microcrystalline, for the crystals cannot be made larger by heating to a higher temperature owing to decomposition. In the other oxides large crystals can be obtained by use of a mineraliser,

[1] Cf. *Ann. Rep. Chem. Soc.*, 1925, 22, 242.

i.e. a substance in the presence of which, either by an intermediate reaction or by solution, "amorphous" precipitates are converted to larger individual crystals. In this group the solvents mentioned above serve as mineralisers, as do fused alkali chlorides, borax, metaphosphates, alkali tungstates, etc. A stream of hydrofluoric acid vapour is an excellent mineraliser, probably owing to formation of the tetrafluoride. The skeleton of silica, which is formed when silicates are fused with microcosmic salt, consists of tridymite, which separates after the metaphosphate has abstracted the bases of the silicate. The silica dissolves in the phosphate on heating, and crystallises again on cooling. The borax bead does not give the skeleton, since borosilicates are formed and not silica itself. Tin dioxide behaves similarly in this respect.

Amorphous forms of the dioxides are obtained by burning the elements; when tin is burned the "tin ashes" (flores stanni) exhibit no crystalline form, and the same applies to the dioxides of silicon and germanium obtained in this way. The oxides are first formed as aerosols, for the elements vaporise at first, and are oxidised when in the monatomic condition. The oxides can thus be obtained as very loose powders. Tin or germanium sulphides also give an amorphous powder of the dioxide on roasting, for here the dioxide formation takes place molecule by molecule, and the molecules are fixed and cannot displace one another to form crystals. These amorphous forms are comparable with amorphous carbon. (*Cf.* p. 141.)

Another form is obtained when the hydroxide is dehydrated. Pieces with conchoidal fracture containing a fair amount of water are often formed in this way, especially in silicon dioxide (opal, mother of pearl). The smaller particles of the amorphous varieties can be made to separate more or less easily by liquid dispersion media, and thus brought into the liquid colloidal state, whereas the crystalline varieties are almost completely insoluble in water, showing that in the latter the internal arrangement of the particles is radically different —the crystalline varieties are formed from single large molecules, while the amorphous aggregates are composed of smaller collections of molecules, which separate from each other with greater ease. Germanium dioxide forms emulsions on contact with water, which are completely cleared on heating, but do not separate on cooling. Thorium and zirconium dioxides, which may be prepared at lower temperatures, *e.g.* by heating the nitrate or oxalate, do not go into colloidal solutions in water without the addition of another substance, but may be peptised by the addition of electrolytes (*cf.* pp. 102, 818). The use of ThO_2 and ZrO_2 as incandescent mantles is discussed on p. 419. The thorium dioxide in incandescent mantles is formed by heating the nitrate.

All these dioxides are very resistant to the action of chemical reagents, especially when crystalline. They can be dissolved by alkalis as they are anhydrides. Acids act on them only with difficulty, although

the dioxides of higher molecular weight can also act as basic oxides ; silicon dioxide is attacked only by hydrofluoric acid, SiF_4 being formed (*cf.* p. 778), but the oxides of elements of higher atomic weight may be brought into solution as sulphates by heating with concentrated sulphuric acid—more easily when they have not previously been strongly heated.

The Hydroxides.—The hydrates of these dioxides are not obtainable by direct addition of water to the crystalline oxides, but may be prepared in other ways. They are specially characterised by their colloidal condition (*cf.* the original works of Kühn[1] and especially of Graham[2]). They are weaker acids than carbonic acid, for as in similar series in the periodic system the electronegative character gradually decreases with increasing atomic weight. The hydroxides of the heavier metals of this group are amphoteric, acting also as bases and forming salts with strong acids. In thorium hydroxide the acidic properties are almost lacking. Like the acid character, the basic character of all these compounds is exceptionally weak, as may be expected from the position of the elements in the middle group of the periodic system, and for this reason all their salts show a strong tendency to hydrolyse, which makes it possible to obtain from them colloidal solutions of the hydroxides. Silicic acid is the strongest of these acids, its colloidal solution being noticeably sour, though as an acid it is exceptionally weak. Its alkali salts are hydrolysed to a high degree; this is shown by the fact that the heat of neutralisation of the dilute acid solution with caustic soda is almost nil, and that the conductivity of the solution obtained is almost equivalent to that of the caustic soda present; in a $N/48$ solution the hydrolysis of the sodium salt may be taken as practically complete. In a solution of sodium silicate there are thus present both free sodium hydroxide and colloidal silicic acid, and as the sodium hydroxide may be removed by dialysis, this method provides a means of preparing pure solutions of silicic acid. It may be directly applied to the other acids of this group : sodium stannate, titanate, zirconate, etc., on hydrolysis, all give rise to colloidal solutions of the corresponding acids, which remain completely clear. Similarly, clear solutions may be obtained by the dialysis of the salts of these elements with acids : zirconium or thorium nitrates on dialysis give very stable and quite clear sols of zirconium and thorium hydroxides.[3]

Conditions of Precipitation.—The hydroxides can be obtained by decomposing the salts with bases or with acids:

$$Sn(SO_4)_2 + 4NaOH \longrightarrow Sn(OH)_4 + 2Na_2SO_4,$$
$$Si(ONa)_4 + 4HCl \longrightarrow Si(OH)_4 + 4HCl.$$
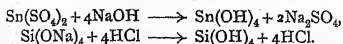
[1] *J. prakt. Chem.,* 1853, 59, 1.
[2] *Phil. Trans.,* 1861, 150, 204 ; *Ann.,* 1862, 121, 1 ; 1864, 123, 529.
[3] Biltz, *Ber.,* 1902, 35, 4431.

The extent of the hydration does not necessarily correspond to these formulae.

In this way the hydroxides are frequently obtained not in colloidal solution but as gels; whether they remain clear sols or gelatinise depends partly on the concentration of the solutions. If, for example, a 10 per cent. sodium silicate solution is poured into a hydrochloric acid solution of a similar concentration, with shaking, a clear sol is obtained, which may be freed from sodium chloride by dialysis. In the same way clear dialysable solutions of stannic acid may be obtained from $SnCl_4$ and sodium hydroxide, but at other concentrations the liquid sets immediately. With thorium salts, in which the hydroxide acts only as a base and never as an acid, a gelatinous precipitate is always formed with alkaline hydroxides or ammonia. These hydroxides sometimes dissolve again in the excess of precipitating medium (except thorium), or they may be peptised to clear solutions by washing with very small quantities of ammonia (stannic hydroxide, cf. p. 102).

Only in the case of silicic acid do there appear to be acids of low molecular weight present when first formed, polymerisation taking place later on. This can be demonstrated by adding hydrochloric acid to water glass, when the freezing point of the mixture shows a gradual rise with lapse of time, and in the early stages considerable quantities of silicic acid pass through a dialysing membrane.[1] Willstätter, Kraut and Lobinger[2] have shown that the rate of polymerisation of silicic acid is dependent on the hydrogen ion concentration. When silicon tetrachloride is hydrolysed polymerisation takes place immediately, owing to the hydrochloric acid simultaneously formed. If, however, silver oxide is present in the water into which the $SiCl_4$ is passed, so that the pH is maintained at 2-2.5, a liquid is obtained which is shown by the freezing point to contain up to 80 per cent. of unimolecular silicic acid, and, if the HCl is completely removed a solution of disilicic acid is obtained. The latter acid, to which the formula $O[Si(OH)_3]_2$ has been given, passes completely and rapidly through the dialysing membrane; acids which result from further dehydration also diffuse through, but more slowly. The mutual precipitation of egg albumin and silicic acid takes place only with acids above the hexasilicic stage.

Schwarz and Richter[3] have proved in other ways the individuality of two hydrates of silica, the highly polymerised and insoluble meta-silicic acid, H_2SiO_3, and the disilicic acid, $H_2Si_2O_5$. If the sodium salts of these acids are made synthetically and then decomposed with concentrated sulphuric acid, the products differ not only in the course

[1] Mylius and Groschuff, Ber., 1906, 39, 116.
[2] Ber., 1928, 61, 2280.
[3] Ber., 1927, 60, 2263; 1929, 62, 31.

of the dehydration curve, but also in the X-radiograms which show the meta-acid to be amorphous, while the di-acid is crystalline (*cf* Gutbier, Hüttig and Döbling, p. 821). When silicic acid gels are made by the hydrolysis of silicon halides at o°, they contain, according to Schwarz and Richter, the hydrate $[SiO_2 . H_2O]_x$. If the formation of the silicic acid takes place in a non-aqueous medium (ether) according to the equation :

$$SiCl_4 + 4(C_6H_5)_3C.OH \longrightarrow Si(OH)_4 + 4(C_6H_5)_3C.Cl,$$
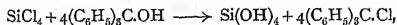
the precipitates obtained[1] contain only a little more water than is required by the formula $[SiO_2 . H_2O]_x$, but are apparently to be regarded as dehydration products derived from several molecules of silicic acid, *e.g.* $(HO)_3Si—O—[Si(OH)_2]_n—O—Si(OH)_3$.

The gels formed by precipitation always adsorb some of the electrolyte which was previously present in the solution. This may be removed with varying difficulty. Thus the gel obtained by dialysis from a solution of sodium silicate decomposed by hydrochloric acid may easily be freed from chloride, but only with the greatest difficulty from sodium, so that the idea that a sodium compound is present is always cropping up. Sols may be obtained entirely free from alkali by boiling a silicic ester with water:

$$Si(OC_2H_5)_4 + 4H_2O \longrightarrow Si(OH)_4 + 4C_2H_5OH ;$$
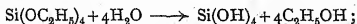
they gelatinise on evaporation. The concentration of this sol is always greater than that obtained in the presence of electrolytes, and may rise to 14 per cent. of silicic acid, without gel formation taking place immediately. The gelatinisation naturally sets in more easily the more concentrated the solution and the higher the working temperature. Gels can therefore be obtained by evaporation of more concentrated solutions (*e.g.* of titanic acid, stannic acid, etc.), but sometimes the stability of the sol is so great that it does not set but dries to a gummy mass, which finally becomes a glassy solid (tin and thorium dioxides).

The silicic acid sol is not coagulated by acids, but is rendered more stable. Salts and alkalis usually accelerate coagulation, though occasionally no coagulation takes place immediately, but precipitation is somewhat accelerated as compared with that in a sol poorer in salts. On the other hand, certain forms of stannic acid are very unstable to added electrolytes, while others are as insensitive as silicic acid. Thorium hydroxide sol is quite stable to electrolytes.

Peptisation.—The purified gels of these compounds may be peptised by the addition of electrolytes ; *e.g.* a pure silicic acid gel redissolves on addition of a little alkali ; thorium hydroxide is peptised from the

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[1] Dilthey, Hölterhoff and Nagel, *Ber.*, 1929, **62**, 24 ; *J. prak. Chem.*, 1931, **129**, 178.

precipitated condition on the addition of a little hydrochloric acid, but only to a turbid liquid; and stannic acid, which has been obtained by oxidising a stannous chloride solution with air and washing the already gelatinising colloid, gives an exceptionally stable sol on the addition of very small quantities of ammonia. The gels become either insoluble or very nearly so only when they have previously been completely dried. The lacquer-like residue of evaporated thorium hydroxide swells up in water, and may be peptised with alkali, but the amount of alkali necessary increases with the compactness of the solid, and less alkali is necessary for peptisation in the freshly precipitated condition than after long standing.

The formation of thorium hydroxide sol is still more interesting, as it may be prepared from the ignited oxide, if the temperature of heating is not too high. A suitable oxide is obtained by heating the oxalate. The melting point of thorium oxide is exceptionally high, so that it is unlikely that sintering takes place at a temperature of 600°, which need not be exceeded for the decomposition of thorium oxalate. The individual particles are deposited as from the aerosol condition, and are not attached to one another. If an oxide prepared in this way is treated with a little hydrochloric acid it goes into colloidal solution—probably as a result of the ionisation of one of the individual molecules which are present in the gigantic molecule formed by a grain of thorium oxide; this ionisation affords the electric charge necessary for colloid formation (*cf.* p. 102). This is a good example of the variation in the properties of these substances with different methods of formation; the ability to give a colloidal solution is lost if the particles on account of previous treatment are in too close contact.

The gels prepared by the wet method also show varying solubility according to the way in which they are made. That of stannic acid is soluble after washing, if it has been precipitated by salts or by bases, but not after precipitation by acids. Thorium hydroxide sol varies in appearance, from a completely clear liquid to a very turbid milky solution, according to the substance from which it is made. Titanic acid gel precipitates in smaller particles in the cold than when heated, and the finer gel is transformed into a coarser one on heating.

Special Properties of Stannic Acid.—An α- and a β- (meta-) stannic acid can be differentiated, the first generally having the greater solubility. α-Stannic acid is formed as a voluminous precipitate when stannic chloride is decomposed by alkali. It is easily soluble in acids, in excess alkali, and even in alkali carbonates, and its solution is not precipitated by a cold solution of alkali sulphate. On the other hand, β-stannic acid is formed as a much less voluminous powder when metallic tin is treated with concentrated nitric acid, and, unlike the α-acid, it is insoluble in acids,

concentrated alkali hydroxide or alkali carbonate; it is easily pre-
cipitated from solution by cold alkali sulphate.   Mecklenburg,[1] in
particular, has shown that they do not act as chemically different acids,
but as substances in which the relationship between the primary
particles themselves is different.   It is important to notice that there
are many intermediate forms between the α- and β-acids: the α- can
also be converted into the β-acid, but not the β- into the α-acid; the
β-acid is the more stable form.   Gels prepared at different tem-
peratures by hydrolysis of stannic salts with water have the properties
of the α- or β-acid, according to the temperature at which they are
prepared.   A typical α-acid is obtained when a solution of stannic
sulphate in water is added to concentrated sulphuric acid at 0°;
but the higher the temperature at which the solution is added the
nearer the product of hydrolysis approaches the β-acid in its properties,
until at about 60° a typical β-acid is formed.   At still higher tempera-
tures of precipitation the gels obtained differ still more from the α-acid,
and those obtained by the oxidation of tin with nitric acid lie beyond
the β-acid stage.   The α-acid may also be converted into the β- by
subsequent heating.

There is no difference in the water content of the two acids.   There
are forms of the α-acid which contain more water than the β-acid,
and some which contain less—temperature exerts no marked influence.
But rise in temperature always tends to increase the size of the
particles, and herein lies one of the most important distinctions between
the α- and the β-forms; the β-acid contains the larger aggregates.
This may be shown, for example, by the differing adsorptive power of
the two acids for electrolytes.   The adsorption of phosphoric acid by
stannic acid is well known, and this property is used for the removal
of phosphoric acid in qualitative analysis.   The power of adsorbing
phosphoric acid diminishes continuously with rise in the temperature
at which the acid is prepared, and as the power of adsorption is a
function of the surface the development of the surface must diminish
with the temperature of formation.   However, the greater size of
the particles alone cannot possibly explain the different properties
of the stannic acids.   A more important factor is the distance of the
particles from each other, and simple filtration makes the gel much
less rapidly peptised.   The chemical elimination of water does not
then take place, but only the mechanical draining-off of the medium.
Colloid chemists do not consider that the great size and arrangement
of the particles is the only cause of the difference in the behaviour
of the gels; the probability of simultaneous chemical differences still
exists and has been proved in the case of silicic acid.   Zirconium
hydroxide shows the same gradations as stannic hydroxide, perhaps
even more markedly; it has a form which on heating to 300° glows

[1] Z. anorg. Chem., 1912, 74, 207.

visibly, and is transformed to another, coarser form—"metazirconic acid." The change in the structure of the gel occurs suddenly, and is so considerable that it can scarcely be regarded as merely mechanical.

The question of the different stannic acids has been investigated by Gutbier, Hüttig and Döbling[1] by the application of the X-ray method. Freshly made precipitates show no interference, indicating an irregular arrangement of molecules. With increasing age the spectrum of anhydrous SnO_2 becomes clearer and clearer. Under all conditions the formation of the anhydrous oxide is gradual and there is no indication of any sudden change. The dehydration curve (*cf.* p. 822) also gives no indication of the existence of definite hydrates. In view of this new evidence, the existence of different stannic acids (mono-, oligo-, and poly-) becomes still more doubtful.

The general conclusion from the work of the above authors is that in all these oxide-water systems there are two tendencies: the formation of purely chemical compounds of stoichiometrical composition, and the formation of colloidal substances of continuously variable composition. The actual properties of the hydroxides result from the operation of these two factors in varying proportions, the former being more dominant in compounds of elements at the two ends of the periodic system, the latter of those situated in the middle.

Gel Structure, with Special Reference to Silicic Acid.—Van Bemmelen[2] first showed that in the gel of silicic acid its properties were not merely dependent upon its water content. He determined the vapour tension of gels containing varying quantities of water by keeping them over sulphuric acid of a known concentration (and hence of known water vapour pressure), and assumed the vapour tension of the gel to be equal to that of the sulphuric acid, when it only diminished very slightly in weight after being kept over this acid for a long time. He dehydrated different gels by allowing them to stand over sulphuric acid, and afterwards tried to rehydrate them by placing them over sulphuric acid of a higher water content. From this he concluded that dehydration and rehydration were not always reversible processes. The gels of these acids can be extremely rich in water, in contrast to some of those of the metals, and silicic acid gel contains, in the most favourable conditions, 330 mols. water to 1 mol. SiO_2; some of the water may be separated by mechanical pressure. It can easily be cut when it contains 30 mols. water, with 10 mols. water it is crumbly, and with 6 mols. water it may be triturated to a fine powder.

In the accompanying diagram, which is typical of those obtained

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[1] *Ber.*, 1926, **59**, 1232.

[2] Mainly *Z. anorg. Chem.*, 1880-1909; see also "Die Absorption," Dresden, 1910.

in these experiments, the water vapour pressures are plotted as ordinates, and the water content of the gels on the abscissae. If we begin at A_0 with the dehydration of a silicic acid gel containing a great deal of water, the vapour pressure diminishes with the withdrawal of the water, until the point O is reached. This seems to be a break in the curve, and owing to the existence of this a definite hydrate was supposed to exist. However, it will be seen that its position may be
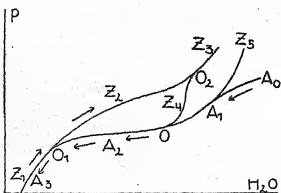
Fig. 64.—The drying and rehydration of silicic acid gel.

quite different from O, and may be more or less displaced towards the left at will, so that it does not possess the properties of a multiple point. The gel, which was transparent up to this point, begins to become milky at O. The turbidity first increases, then diminishes, and has again completely vanished at O_1. Van Bemmelen indicates the points O and O_1 as "transition points." Between these two transition points the withdrawal of water is completed with little change of vapour pressure, i.e. a slight change in pressure here would give rise to considerable loss of water. If the second transition point is passed on further lowering the pressure, the loss of water becomes relatively much less, the curve bends downwards and ends in the product A_8, which contains but little water.

On placing the product A_8 in a damper atmosphere, rehydration begins (Z curve). From A_8 to O_1 the process of rehydration corresponds exactly to the previous dehydration. The reversibility ceases at the point O_1; increased vapour pressure leads to products poorer in water (curve Z_2) than would be obtained in the path of dehydration at the same vapour pressure; it is true that the increase in water content becomes somewhat greater with increasing pressure at a later stage, but a higher pressure must always be applied for rehydration than is necessary to reach a similar dehydrated product. The point on Z_3 at which the turbidity again vanishes (O_2) lies much higher than that (O) at which it previously set in. If hydration proceeds beyond this point water is still taken up, but never so much that a product with 300 mols. H_2O is obtained (curve Z_8). Also, if the dehydration is stopped at point O on the curve, without dehydrating further, and then hydration begun, path A is not taken, but Z_4, which joins the general rehydration curve. Even if O is never reached on dehydration, e.g. at point A_1, rehydration does not lead to A_0 again but to Z_5. The portion of curve O_1A_8 is thus the only reversible part.

Silicic acid gels do not all show the same dehydration curve

throughout, nor the same positions of the transition points. Their positions depend much more on other factors, *e.g.* the method of preparation of the gel, its age, the velocity of dehydration, besides the temperature of dehydration. The point O is reached later (*i.e.* lies so much further to the left) when the gel is precipitated from a more dilute solution, or more quickly dehydrated, or is less aged, or is dehydrated at a lower temperature. If the point O lies very close to O_1 the A curve lies almost on the Z curve. Silicic acid which has been heated to redness for a long time generally shows no further resorption, and the Z curve is non-existent.

It is obvious from this that the transition points are not transformation points in the sense of the Phase Rule, and the general opinion is that the water is mostly held, not in chemical combination, but by adsorption, since the union is stronger the less water there is present. The method of adsorption is, however, not the same for the water firmly attached as for that more loosely bound, as is shown by the existence of transition points.

Silica gel adsorbs vapours other than water vapour and this property is utilised in the recovery of solvent vapours when diluted with large volumes of air or other gases.

A silicic acid gel prepared from very dilute solution appears to be flocculent, and later, granular, when observed in the ultramicroscope. The honeycomb structures which best explain the enclosure of water cannot be confirmed. If, however, it is dried it begins to become turbid when it contains 40 per cent. of water; the turbidity vanishes again on drying further. If the clear gel so obtained is now saturated with a liquid such as benzene the structure which has since become honeycombed becomes distinctly visible. It is remarkable that the visibility of the structure only appears in this middle stage when it is partly filled with liquid, but not when the gel is very empty, nor when it is very full. This fact was explained a long time ago by Bütschli on the assumption that in this middle stage, although the walls of the comb are still covered with liquid, the inner spaces already contained air, and the different refractive powers of the air and the moist walls made them visible. As soon as the honeycombs are completely filled with liquid their structure becomes invisible, and similarly when the liquid has completely dried from the walls. Zsigmondy, however, quite reasonably doubted whether invisibility can occur under the latter conditions. The dried gel appears pure white and opaque owing to the difference in refractive power of dry wall and air, like kaolin, which has a similar structure. The region of turbidity may be that in which, in some places, liquid is present, and in others its vapour, the turbidity being due to the difference between the refractive index of the vapour and of the liquid. On the assumption of discontinuous liquid content in the gel, it is necessary to explain why the Z curve in the diagram on p. 822 lies above the A curve. It was previously assumed that the gel underwent a contraction, which was not completely nullified on rehydration, so that a greater pressure was necessary in order to fill the cells to their previous capacity. Besides this partially correct explanation, another factor comes into play—that the liquid meniscus which is formed when a liquid ascends (path Z) a wet capillary is more curved than that which is formed when a liquid descends a similar capillary (path A). Now, the vapour pressure at the curved meniscus is greater than that at the plane one, and therefore a greater external

vapour pressure must be present to permit of the formation of the very curved
meniscus. There are also many other factors which act in lowering the vapour
pressure of gels ; besides the capillary depression of vapour pressure, there arises
the question of lowering of pressure caused by chemical union, by solution of non-
volatile substances, as well as by adsorption.

The general question of the structure of gels is not yet clear.[1] Most workers
hold that they are solid-liquid systems in which either a discontinuous granular solid
phase is dispersed through the liquid, or the solid part takes the form of minute
fibrils forming a continuous matted structure. In many gels (*e.g.* in the organogels
of dibenzoyl cystine[2] and of calcium acetate[3]) recrystallisation takes place with
formation of large crystals of the solid phase. Silica gel shows the crystalline
structure of cristobalite[4] when heated for some hours above $115°$. Silicic acid gels
moreover, are not typical of gels in general, as the sol-gel transformation is not
noticeably affected by temperature and is irreversible.

Protective Action.—The coarse structure of gels causes the "mole-
cular weight" of the hydroxides as sols to appear to be very high.
Thus silicic acid sols give numbers of the order of 50,000. Silicic acid
sol has almost no protective effect on metal sols. Stannic acid, on the
other hand, can exert a considerable protective action in colloidal gold
solutions, and a colloidal gold solution with stannic acid as protective
colloid gives rise to "Purple of Cassius" (*cf.* p. 108), which is obtained
by the action of stannous chloride on solutions of gold chloride. It
serves as a way of recognising the presence of gold, and may be
precipitated in the solid form by electrolytes. If the stannic acid
is again peptised by very small quantities of ammonia (*cf.* p. 819) the
gold likewise goes into solution and gives a coloured liquid, which
resembles in many ways a solution of an organic dyestuff. Ultramicro-
scopical examination shows the gold particles quite clearly visible.
Purple of Cassius also shows a typical gold lattice when examined by
X-rays. Purples of silver and platinum can be similarly obtained.

If silicic acid sol is added to a sol containing oppositely charged
particles, mutual precipitation occurs owing to neutralisation of the
electric charges. Glue, alumina or iron hydroxide act as precipitants in
this way. Silicic acid, like stannic acid, is a negatively charged colloid,
while zirconium and thorium hydroxides are positively charged.
Germanium hydroxide is similar in properties to those already discussed.
It may easily be precipitated, and again peptised to clear or turbid
solutions. Colloidal solutions of lead dioxide are not known.

Silicates, Stannates, etc.—Fresh silicic acid dissolves in caustic
alkalis, and alkali salts can be obtained by fusing the dioxides with
alkali hydroxides or carbonates, but the carbonic acid is only partially
removed from the carbonate if care is not taken to remove it from the

[1] *Cf.* D. J. Lloyd, article in *Colloid Chemistry*, vol. i., New York, 1926.
[2] Wolf and Rideal, *Biochem. J.*, 1922, 16, 548.
[3] Thorne and Smith, *Kolloid Z.*, 1929, 48, 113.
[4] Krejci and Ott, *J. Phys. Chem.*, 1931, 38, 2061.

surrounding atmosphere. On treating the melt with water a very considerable decomposition takes place. Thus fused alkali silicate (water glass) may be completely dissolved on long heating with water, but the solution contains silicic acid peptised by alkali, as well as free alkali. It is completely decomposed by carbonic acid and the silicic acid precipitated. If it is treated with salts of heavy metals very voluminous slimy precipitates containing silicic acid and the heavy metal are obtained, but it is probable that not much of the true heavy metal silicate is present. Silicic acid which has been heated to red heat is scarcely soluble in solutions of alkali hydroxides. In the absence of water, however, the preparation of definite silicates is possible. Those of simple composition crystallise quite well from a melt containing calculated quantities of the components, but silicates of complicated composition either crystallise with difficulty or not at all, and solidify on slow cooling to a glassy or slag-like mass. They have no definite melting point, but gradually soften, and the solidifying point of the natural silicates does not coincide with their softening or melting points, which lie round about 1200° (*cf.* p. 195 for the fusibility of silicates). The absence of a definite melting point proves that decomposition occurs on melting, and suggests that the composition of even the apparently simple silicates is complex. The extraordinary variety in composition of the natural silicates is in accordance with this.

Structure of Silicates.—Attempts have been made to create order in this large class of compounds by considering them as derivatives of silicic acids of different degrees of dehydration—salts of "polysilicic acids." Mono-, di-, tri-silicates, etc., are distinguishable, which are thus derived from the acids:

Monosilicic acid .	H_4SiO_4 or H_2SiO_3	*i.e.*	$H_4SiO_4 - H_2O$.
Disilicic acid .	$H_6Si_2O_7$	,,	$2H_4SiO_4 - H_2O$.
Trisilicic acid .	$H_8Si_3O_{10}$	,,	$3H_4SiO_4 - 2H_2O$, etc.,

and from acids which are derived from several molecules of silicic acid by different methods of dehydration. This systematic arrangement of the natural silicates is unsatisfactory from the chemical point of view. The chemistry of the silicates presents peculiar difficulties which make it very hard to study this group of compounds. Their high melting point, their insolubility in indifferent solvents and their chemical inertia—a consequence of their high ionic charges—combine to make them one of the least satisfactory groups in inorganic chemistry. Attempts such as that of Jakob[1] or Wahl[2] to bring the silicates in line with Werner's theory of complex structure have insufficient experimental

[1] *Helv. Chim. Acta*, 1920, 3, 669.

[2] *Z. Kryst.*, 1927, 66. 33, 173.

basis owing to the impossibility of being certain of individual molecules. The valuable investigations of V. M. Goldschmidt[1] are more fruitful. He has succeeded in explaining the structure of silicates, by considerations of isomorphism, derived from the preparation of soluble compounds isomorphic with silicates and yet consisting entirely of elements other than those present in true silicates (see p. 829).
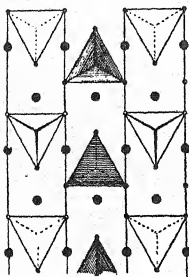
FIG. 65.—Olivine.

W. L. Bragg[2] succeeded in elucidating the structure of silicates by means of X-ray analysis. This very important advance has brought the silicate problem nearer solution. One result of Bragg's research is that it is no longer possible with the majority of silicates to speak of an isolated molecule, and hence the usual formulae cannot give a true representation of the structure. The principal results of his comprehensive researches, together with some extensions resulting from the work of Pauling and his collaborators, are as follows :—

The results of Bragg indicated that in general we must regard the silicates as consisting of positively charged Si^{++++} and negative $O^=$ ions. This agrees with the electronegativity scale of the elements, which requires that the bond between silicon and oxygen should be mainly ionic. While ordinary oxy-salts contain individual groups such as PO_4''', SO_4'', ClO_4', which combine with metallic ions to give distinct molecules, such groupings exist in but few silicates, but are found in the orthosilicates, the olivine (Fig. 65), chondronite and phenacite (Fig. 67) groups. The other silicates are composed of uniform continuous linkages of Si and O ions in regular arrangements, which give scope for almost unlimited extension, and from which smaller groups can no more be separated than groups containing carbon can be separated from carbon chains in organic compounds; with this difference that it is not single atoms coupled together, but two ions, Si^{4+} and O^{2-}.

All silicates have this in common, that a silicon ion is surrounded by four oxygen ions, which are always 1·62 Å distant from it, the oxygen atoms themselves being always separated by a distance of 2·6-2·8 Å. The electrons are mostly under the influence of the silicon ion, but the behaviour of the whole group is determined by the equal distribution of the four negative charges among the four oxygen ions.

FIG. 66.—Arrangements of SiO_4 tetrahedra.

So long as the SiO_4 groups are not independent, as in the orthosilicates, there are

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[1] *Geochemische Verteilungsgesetze*, viii, Oslo, 1926.
[2] *The Structure of Silicates*, 2nd ed., Leipzig, 1932.

two ways in which the oxygen ion can be attached to the silicon ion. In one, the oxygen shares its valency with the two silicon ions—that is, it may be supposed to take up a position between the contiguous apices of two tetrahedra. In this position the oxygen has no free valency and hence is fully saturated towards other ions, the linkage being homopolar as in the linkage of carbon in organic chains.

Si above   Be. above

Si below   Be below
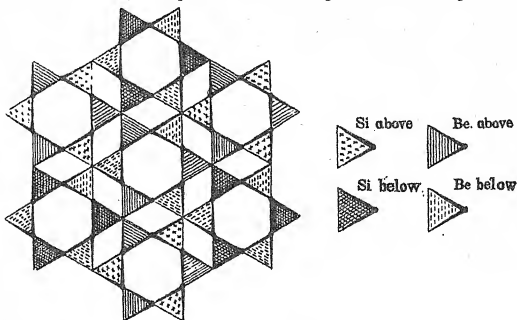
FIG. 67.—Phenacite.

Alternatively, the oxygen ion may be joined to a single silicon ion, when it will carry a negative charge and can neutralise metal ions.

It is possible to distinguish four types of combination, all of which result from various tetrahedral arrangements:

(a) *Independent Groups* of the type $(Si_2O_7)^{VI}$, $: (Si_3O_9)^{VI}$, $(Si_4O_{12})^{VIII}$, or $(Si_6O_{18})^{XII}$. In these the attachment of two tetrahedra takes place through an oxygen ion, which forms a common apex. The diorthosilicates provide examples of this; in

FIG. 68.—Pyroxene.

these one such group consists of two tetrahedra. In beryl, $Be_3Al_2Si_6O_{18}$, there are six tetrahedra linked together at the corners to produce a ring formation.

(b) *Silicon-oxygen Chains.*—In these two oxygen ions are common to two tetrahedra, the empirical formulae of the radicals being $(SiO_3)^{II}$ and $(Si_4O_{11})^{VI}$. The pyroxenes, (Fig. 68) *e.g.* diopside, $MgCa(SiO_3)_2$, provide examples of this structure. By further condensation two such chains can be made to link together so as to be side by side as in the amphiboles (Fig. 69), which have the radical $(Si_4O_{11})^{VI}$ as a basis. If these groups, in which the radicals are arranged side by side, link up, a chain is obtained. Such a chain gives us group (c) (Fig. 66).

(c) *Silicon-oxygen Layers*, exemplified in mica (Fig. 70) and formed by the cross-linking of chains. Three oxygen ions of each tetrahedron belong to a neighbouring tetrahedron, whilst the fourth has a free valency. The oxygen-silicon proportion is shown by the radical $(Si_2O_5)^{II}$. A still more complex network is found in the tetragonal arrangement of the tetrahedron as in apophyllite (Fig. 71).

(d) *Three-dimensional Silicon-oxygen Lattice*, as in the solid modifications of

silica. In this lattice the silicon ion can be partially replaced by aluminium producing a negative lattice, which may be regarded as an enlarged acid radical, into which exchangeable metallic radicals can be introduced, as in the zeolites (p. 830).

In all these classes the linkage of the Si-O groups takes place through the metal ions. As yet, however, one must proceed arbitrarily when one wishes to isolate definite Si-O complexes, although even this can only be accurately done by utilising the above classification. There is still the possibility of regarding these complexes as units. With the metal ion each of those of small ionic radius is surrounded by
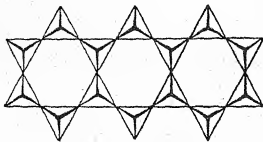
FIG. 69.—Amphibole.
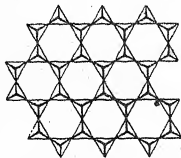
FIG. 70.—Mica.
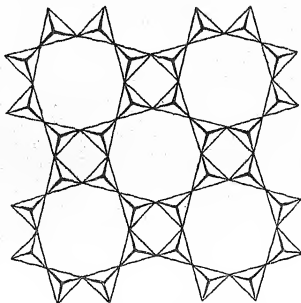
FIG. 71.—Apophyllite.

a small number of oxygen ions, and the group has a regular form. With larger cations (Na', K', Ca'') co-ordination leads to such irregular forms that one can no longer speak of individual groups.

The observed co-ordination numbers of the oxygen ion with metal ions are as follows:

Be'' 4	B''' 3, 4	Na' 6, 8	Mg'' 4, 6, 8
Al''' 4, 5, 6	Si'''' 4	Ca'' 6, 7, 8	Sc''' 6
Ti'''' 6	Mn'' 4, 6, 8	Fe'' 4, 6, 8	Fe''' 4 ? 6
Zn'' 4	Zr'''' 8	Ba'' 6, 12	

It is remarkable that aluminium as well as silicon can replace not only bivalent metals, but also each other.

When isomorphous replacements take place, the number of oxygen ions as well as of F' or OH' radicals in the elementary unit remains constant. If the number of oxygen ions becomes greater or less the arrangement becomes upset, so that each type of structure is derived from the characteristic number of oxygen ions. The oxygen lattice may thus be regarded as the primary; and Bragg regards the silicate as a structure of oxygen ions that are distant from one another by about 2·7 Å, and

between which is space for a definite number of metal or silicon ions, which can fill these in different proportions. Besides the replacement of one element by another of similar valency in the structure, the spaces may be occupied by elements of different valency as when NaSi replaces CaAl in the felspars. Aluminium can replace silicon or magnesium with equal ease, and magnesium, manganese and iron are interchangeable. Calcium replaces sodium, as potassium replaces barium. Provided always that the sum of positive and negative valencies is zero, a great number of variations can take place in the crystals and produce the huge variety of minerals belonging to the same family.

Isomorphism.—In the study of the structure of the silicates the important work of V. M. Goldschmidt[1] referred to above must be considered. Substances of analogous chemical formula which show similar crystal structure are described as isomorphous. The analogy in chemical structure is not disturbed if ions are replaced by chemically similar radicals, *e.g.* K by NH_4 or Cl by CN. Analogy in crystal structure is best determined by X-ray analysis. According to Goldschmidt, isomorphism appears when the relative size of the crystal unit and the relative strength of polarisation (*cf.* p. 236) between certain limits are equal for the two substances in question. The possible arrangements of the crystal units in the crystal cause certain structures to be bound up with the determined relations of the size of the crystal units. Thus the ion lattices of the type RX_2 in the fluorite type appear in the rutile type as the so-called layer lattice. The first type is found when the ratio of the ionic radii R : X is greater than 0·67, the second when it is less than 0·67, the third when the ratio is less than 0·4-0·5 or if the ion X is strongly polarisable. On the basis of these facts crystals of any form can be produced at will when the ion sizes as determined by Goldschmidt are known (pp. 36-37). It is a matter of indifference whether the ion X is univalent or bivalent and the law holds equally well for halides of formula MF_2 and for dioxides of formula MO_2. In the same way, by selection of the size and polarisability of the units, compounds of formula MX can be obtained in crystals of the zinc blende type, the würtzite type or the caesium chloride type.

These relations still hold when the ions are replaced by radicals. Thus $NiCl_2$ crystallises in a layer lattice, as the ratio of the (apparent) radii Ni : Cl is 0·4, but $[Ni(NH_3)_6]Cl_2$ forms a fluorite lattice, as the radius of the nickel atom is increased by the addition of ammonia molecules and the ratio is thus augmented to 1·41. As the apparent size of the ion is greatly influenced by the polarising power of the ions around it (p. 38) the crystal structure is not entirely dependent on the size of the crystal unit in its isolated form, as was previously supposed, but depends also on the force exerted by neighbouring ions. As this force depends on the valency of these ions (p. 38) it is possible for an ion to replace another of different valency in the lattice, provided that an equalisation of size is thus produced. Hence it is possible to find a compound of structure isomorphous to another in which the valency of the units, and consequently the sum of their valencies, is different. Therefore, in the replacement of one unit by another, the valency must be increased or diminished by a certain amount. The new unit must also on the grounds of size and polarisability be capable of forming a similar crystal. This effect can be seen in the isomorphous $RbBF_4$ and $BaSO_4$, or to quote an example among the silicates, the pair $Li_2BeF_4 - Zn_2SiO_4$. The orthofluoberyllate is thus a model for the willemite-phenacite group. In the same way $NaLiB_2F_6$ forms a model for the diopside pyroxenes :

		Ca	Mg	Si_2	O_6	Na	Li	B_2	F_6
Radii	.	1·06	0·78	0·39	1·32	0·98	0·78	0·34	1·33 Å

The crystal structure is dependent on the relative rather than on the absolute size

[1] *Geochemische Verteilungsgesetze*, viii, Oslo, 1926.

of the crystal components. Two compounds of formula MX_2 will be isomorphous when the quotient of the radii of the anion and cation is within the limits, independently of the sum of these radii. Thus the following three compounds are not isomorphous, in spite of the equality of the sums of the radii :

	BaF_2	$MgBr_2$	US_2
R_a	1·43	0·78	1·05
R_k	1·33	1·96	1·74
$R_a + R_k$	2·76	2·74	2·79 Å

while the following pair are isomorphous, though the sum of the radii is different :

	CaF_2	$SrCl_2$
R_a	1·06	1·27
R_k	1·33	1·81
$R_a + R_k$	2·39	3 08 Å

Isomorphism does not thus depend so much on chemical similarity between the two substances, but is much more a question of the possibility of physical building-up of similar molecular structures.

The formation of mixed crystals is closely connected with the phenomenon of isomorphism. For mixed crystals to be possible, the absolute sizes of the units of the crystal structure must be closely similar, and no greater difference than 15 per cent. between the values of the radii is permissible when these are small. When this condition is fulfilled ions of very different character can replace one another in the crystal lattice, e.g. Cd·· and Ca·· or Pb·· and Sr·· can replace one another in lattices of the simplest kind.

Many silicates contain water. It can be driven off only at a high temperature, and is thus not present as water of crystallisation or adsorption. Other silicates, especially the zeolites, give up part of their water content with quite moderate drying, and then take it up again on being kept in damp air ; here also it does not behave as water of crystallisation, as it shows no definite dissociation pressure, and may perhaps be like the water in the gel of silicic acid in the branch of the curve O_1A_8 (Fig. 64, p. 822).

Silicates are attacked by acids in many different ways. Some are rapidly decomposed by hydrochloric acid even in the cold, when part of the silicic acid separates as a jelly. Others are attacked in the same way, but much more slowly ; others, again, almost completely resist this treatment. In general, the decomposition is more successful the more electropositive the metal contained in the silicate; alkali silicates are easily attacked, alkaline earths less easily, and aluminium and iron silicates still less easily. Concentrated sulphuric acid is better than hydrochloric, since it can be used at a higher temperature. Hydrofluoric acid decomposes all silicates with the formation of SiF_4 (p. 776).

In spite of their great insolubility certain silicates have the curious property of interchanging bases. This is best observed in artificially prepared "permutite," an alkali aluminium silicate of empirical formula $2MO . Al_2O_3$, $3SiO_2 . 2H_2O$, aq., which is similar to zeolite, but not crystalline, and in which the water of crystallisation is not

essentially different from the water of constitution.[1] In the alkali and alkaline earth permutites there are three molecules of water of crystallisation in an atmosphere saturated with vapour. If permutite is treated with liquids containing silver, calcium, manganese, iron or other salts, these take the place of the sodium. This phenomenon is used technically to remove the hardness and the iron from water. The permutite may be regenerated by treatment with sodium chloride solution; the sodium then again enters into its old position, and the metals which replaced it are again displaced. It is probable that the exchange of the bases is not purely chemical, but at least partly a process of adsorption. The problem of the mechanism of base exchange is of considerable importance in the field of colloid chemistry. It is interesting that the replacement ability of the alkali metal ions in permutites coincides with the lyotropic series.

The *ultramarines* are an interesting and important series of sodium aluminium silicates containing sulphur compounds and possibly free sulphur. Their structure is still not accurately known[2] though much attention has been given to it during the last decade. It is almost certain that the ultramarines consist of an aluminosilicate skeleton in which exist replaceable alkali ions as in the permutites. Sodalite, $Na_4Al_3Si_3O_{12}Cl$ contains chloride ions instead of $S_2^=$, whilst the latter may be replaced by selenium and tellurium also. The colour is apparently to be attributed to the Group VI elements, since sodalite is white.

Stannic, titanic, zirconic and plumbic acids form salts which are remarkably stable, much more so than those of silicic acid, although it might be expected that owing to the metallic element in them they would be much less acidic. Si, Ti and Sn, however, have almost identical electronegativity values. In lead dioxide the basic properties are pronounced, $Pb(SO_4)_2$, $K_2Pb(SO_4)_3$ and $Pb(CH_3COO)_4$ being known. The alkali salts and those of the alkaline earths may be obtained quite well crystallised from aqueous solution by using a large excess of alkali; a normal solution of sodium stannate in water is only hydrolysed so that its alkalinity corresponds to a 0·02 N. NaOH solution; hydrolysis is complete in a $N/3000$ solution. It is possible that this is due to the basis of the salts being a complex aquostannic acid, $H_2[Sn(OH)_6]$. The hydrolysis increases with time, partly because the tin hydroxide formed ages, whereby its power of adsorbing alkali also changes.[3] These salts are colourless, including those of plumbic acid, *e.g.* $Na_2[Pb(OH)_6]$. Of the latter, best known is the plumbous salt, $Pb[Pb(OH)_6]$, *i.e.* $Pb_2O_3 . 3H_2O$, which is also known as lead

[1] Günther-Schulze, *Z. Elektrochem.*, 1921, **27**, 402.

[2] *Cf.* J. Hoffmann, *Z. anorg. Chem.*, 1929, **183**, 37 ; Jaeger, *Trans. Faraday Soc.*, 1929, **25**, 320.

[3] Zocher, *Z. anorg. Chem.*, 1920, **112**, 1.

sesquioxide, and is an orange-yellow compound. It is doubtful whether its constitution is different from that of the anhydrous oxide Pb_2O_3, which is formed by heating PbO_2 to $350°$ and may be assumed to be $Pb[PbO_3]$, the plumbous salt of metaplumbic acid. Metaplumbic acid also forms salts with other heavy metals. The salts of orthoplumbic acid, $H_4[PbO_4]$, are more important; they are generally formed by heating bases with litharge in air. They have a sharply defined range of existence and evolve oxygen when heated above this limit. This may be applied to the preparation of oxygen [1]:

$$2CaO + PbO + O \rightleftharpoons Ca_2PbO_4.$$
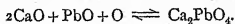
At low temperatures (or high pressures) atmospheric oxygen is absorbed by a mixture of lime and litharge; at higher temperatures (or lower pressures) the oxygen is evolved from the plumbate formed.

Red lead or minium, plumbous orthoplumate, $Pb_2[PbO_4]$, is a bright red substance which exerts an oxygen pressure of $\frac{1}{3}$ atm. at about $550.°$ It is therefore formed when PbO or PbO_2 is heated to this temperature in air. If heated further it is decomposed with the formation of PbO. In pure oxygen the decomposition temperature may be as high as $636°$, since at this temperature the minium has an oxygen pressure of one atmosphere. If these plumbic salts are acted on with nitric acid the base is removed as the nitrate, and the brown $Pb(OH)_4$ or PbO_2 remains. An intermediate oxide between minium and Pb_2O_3—$3PbO$, $2PbO_2$, $3H_2O$—may be formed by the action of H_2O_2 on an alkaline plumbous salt solution, and is distinguished by exceptional reactivity.

Meta- and ortho-plumbates are found in equilibrium in solution. If alkali plumbates are prepared by the electrolytic oxidation of alkali plumbite solutions, or with lead electrodes in caustic soda solution,[2] at a low concentration of the alkali, salts of metaplumbic acid, H_2PbO_3, are formed, or at higher concentration those of orthoplumbic acid, H_4PbO_4. Hence minium, i.e. the lead salt of the ortho-acid, is obtained by mixing solutions of plumbites and plumbates if the solution is strongly alkaline, but Pb_2O_3, i.e. the lead salt of the meta-acid, is formed when it is less alkaline.

Siloxanes.—Siloxanes are silanes in which the hydrogen is partly replaced by oxygen. They are analogous in structure to organic chemical compounds which contain oxygen, such as the acids of carbon, but this analogy is not borne out by their chemical behaviour. They are also distinguished from the carbon compounds by their exceptional ability to polymerise, already found in "sil-dioxane," SiO_2, which, unlike CO_2, is known only in the polymerised form. Only two of

[1] Kassner, Chem. Zeit., 1893, 17, 1242.

[2] Grube, Z. Elektrochem., 1922, 28, 273.

these compounds are obtainable in the monomeric condition [1]: those corresponding to dimethyl ether, $(SiH_3)_2O$, and formaldehyde, $(SiH_2)O$.

All these compounds are formed by very careful hydrolysis of the corresponding halogen silanes, when the halogen is exchanged for oxygen:

$$2SiH_3Br + H_2O \longrightarrow 2HBr + (SiH_3)_2O. \quad \text{Disiloxane.}$$

$$SiH_2Cl_2 + H_2O \longrightarrow 2HCl + (SiH_2)O. \quad \text{Prosiloxane.}$$

$$2SiHCl_3 + 3H_2O \longrightarrow 6HCl + \underset{H}{\overset{O}{Si}}.O.\underset{H}{\overset{O}{Si}} . \quad \text{Silico-formic anhydride (polymerised).}$$

$$Si_2Cl_6 + 4H_2O \longrightarrow 6HCl + SiO_2H.SiO_2H. \quad \text{Silico-oxalic acid (polymerised).}$$

$$Si_3Cl_8 + 5H_2O \longrightarrow 8HCl + SiO_2H.SiO.SiO_2H. \quad \text{Silico-mesoxalic acid (polymerised).}$$
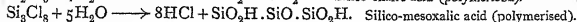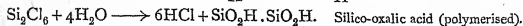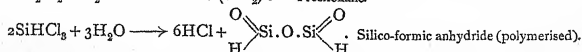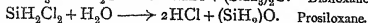
The hydrolysis is thus analogous to that of the halogen carbon compounds, but the latter occurs with much greater difficulty.

The non-polymerised compounds are colourless, odourless gases, and, in contrast to the silanes, are not spontaneously inflammable in air. $(SiH_3)_2O$, however, explodes easily in pure oxygen, and shows no tendency to polymerise. It melts at $-144°$, boils at $-15°$ and can be heated to $250°$ without changing—it decomposes only at red heat. In contrast to this $(SiH_2)O$ polymerises when it is liquefied by cooling, and a volatile portion is formed, which is soluble in benzene and gives a sixfold molecular weight, together with a less volatile, more highly polymerised portion resembling silicic acid. The other siloxanes are known only in the polymerised form. They are voluminous, light, white substances, which increase in instability from the anhydride of silico-formic acid through silico-oxalic to -mesoxalic acid. The silico-formic anhydride may be heated to $300°$ without decomposition, and does not ignite below that temperature. Silico-oxalic acid explodes on warming with the emission of sparks; silico-mesoxalic acid explodes even on slight friction. All are insoluble in water, but dissolve in aqueous alkali with evolution of hydrogen to form silicates: $(SiH_2)O + 2NaOH \longrightarrow Na_2SiO_3 + 2H_2$; $(SiH_3)_2O$ gives hydrogen gradually with water alone. They are mild reducing agents, though the solids may be saturated with concentrated nitric acid without reaction, but permanganate or solutions of noble metals are slowly reduced. $(SiH_3)_2O$ can be converted into $(SiCl_3)_2O$ by chlorination; this chloride and also $Si_4O_4Cl_8$, i.e. $SiCl_2 \underset{O-SiCl_2-O}{\overset{O-SiCl_2-O}{<>}} SiCl_2$, are obtained by the interaction of $SiCl_4$ and oxygen [2] at $800-1000°$. For reactions of the silicon halides with ammonia, see pp. 636-7.

Similar compounds of the other elements of this group are not known at present.

[1] Stock and his pupils, *Ber.*, 1917, 50, 1754, 1764; 1919, 52, 1851.
[2] Rheinboldt and Wisfeld, *Annalen*, 1935, 517, 197.

An interesting group of new silicon compounds, which has been reported recently, consists of resinous polymers containing siloxane linkages. These may be prepared by hydrolysing or oxidising[1] alkyl silicon halides, the condensation being further extended by heating. The resulting gels are hard, brittle and transparent, and are remarkably thermostable. The nature of the resin depends on the ratio of alkyl (usually CH_3) to silicon, and the structure is considered to be :

$$Me_2Si—O—MeSi—O—Me_2Si—O$$
$$|$$
$$O$$
$$|$$
$$Me_2Si—O—MeSi—O—MeSi—O—   \text{etc.}$$
$$|$$
$$O$$
$$|$$
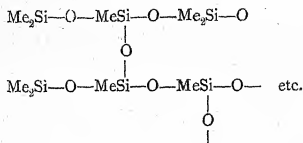
There is evidence of the formation of cyclic trimers in many of the reactions which lead to these substances.

Siloxens.—This type of compound is one of the most interesting known, both from the chemical and the physical points of view.[2] The parent substance is siloxen, $Si_6O_3H_6$, a polymerised siloxane, which is formed when $CaSi_2$ is digested with dilute hydrochloric acid. It is derived from three molecules of the silicide and has the following structural formula :
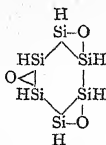
This silicide has all the properties of a highly polymerised substance, but only on one crystal face. On the others it shows an extraordinary reactivity ; the flat six-sided tables are attacked by the acid only on the large faces, the sides of the prisms remaining completely unchanged when the acid is added. In this way the siloxen lamellæ are built up one above the other, the base planes remaining in place while the sides of the prisms crinkle like the sides of an accordion. This effect is similar to that observed in the formation of graphitic acid (p. 143).

The siloxen thus obtained is chemically very active and is a powerful reducing agent. As it catches fire in the air and decomposes water with formation of hydrogen, all manipulations with it must be carried out in dry nitrogen and in the dark. On oxidation a whole series of silicic

[1] Rochow and Gilliam, *J. Amer. Chem. Soc.*, 1941, **63**, 798 ; Hyde and DeLong, *ibid.*, 1194.

[2] Kautsky, *Z. Electrochem.*, 1926, **32**, 349 *et seq.*

acid-siloxen compounds is obtained. The hydrogen in the siloxen can be substituted by halogens atom by atom; for instance:

$$Si_6O_3H_6 + I_2 \longrightarrow Si_6O_3H_5I + HI$$
$$Si_6O_3H_6 + HBr \longrightarrow Si_6O_3H_5Br + H_2$$
$$Si_6O_3H_6 + 3Br_2 \longrightarrow Si_6O_3H_3Br_3 + 3HBr.$$
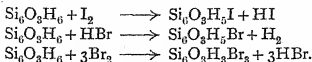
Further substitution gives $Si_6O_3H_2Br_4$ and $Si_6O_3Br_6$. The halogen and acid compounds are greenish to bright yellow in colour, the actual tint depending on the kind, number and position of the substituents. The hydroxy- and amino-compounds formed by reaction of these compounds with water or ammonia are intensely coloured:

$$Si_6O_3H_5Br + H_2O \longrightarrow Si_6O_3H_5OH + HBr$$
$$Si_6O_3H_3Br_3 + 6NH_3 \longrightarrow Si_6O_3H_3(NH_2)_3 + 3NH_4Br.$$
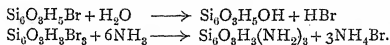
With further substitution the colour deepens to red, brownish violet and finally black. The siloxen ring is a chromophore in which the light absorption is moved into the visible spectrum by the introduction of auxochrome groups, as in organic compounds. These compounds are also remarkable for sensitiveness to light, strong fluorescence and extraordinarily bright chemiluminescence.

When the hydroxy-compounds are treated with acids the hydroxyl group is replaced by the acid radical. These salts are reversibly hydrolysed by water to give the hydroxy-compound. Hence these hydroxy-derivatives react like weak bases, giving salts with such acids as the halogen acids, sulphuric, phosphoric, acetic and formic acids. All other halogen derivatives of silicon are irreversibly hydrolysed by water.

The hydroxysiloxens, and in particular the deep black hexahydroxy-siloxen, which is very explosive, are also formed when the acid derivatives are treated with sulphurous acid; this is itself reduced to hydro-sulphurous acid. In these reactions the siloxen skeleton remains intact and the position of the siloxen rings in the lamellae remains unaltered; but when the hydrogen is completely replaced by chlorine or by treatment with sodium ethoxide the lamellae break up into single molecules of the unimolecular liquids, $Cl_3Si . O . SiCl_3$ and $(CH_3O)_3Si . O . Si(CH_3O)_3$ respectively.

Even more remarkable than these chemical properties are the physical aspects of these reactions. They all take place very quickly and completely, without the solid structure of the substance undergoing any alteration. In some ways this type of reaction is analogous to the permutite changes (p. 830), but with these compounds the changes take place with great rapidity and with a theoretical yield. Kautsky terms this sort of reaction permutoid. Each molecule of the silicon compound gives the proper number of molecules of the product by a process of instantaneous diffusion. It is extremely improbable that solid solutions

of such varied substances as water (which does not even wet them), bromine, ammonia, acetic anhydride, sulphuric acid, etc., are formed with the silicon compounds without alteration in volume. A further argument against the formation of solutions is the fact that excess of any of these reagents can readily be washed out. The progress of the diffusion can be made visible by the use of dyes, and it is then clear that it takes place between the lamellæ and not across them. Kautsky makes the suggestion that the cohesion in the basal planes is much stronger than in the prism faces, so that the thickness of the lamellæ is only 1-2 molecules. Consequently, all the molecules lie on a lamellar surface and so can react readily with an added reagent.

Owing to the enormous surface presented by the siloxens they can adsorb great quantities of gases quite independently of the nature of the derivative which may be used. The high specific surface is also in all probability the cause of the chemiluminescence of these substances. At low temperatures it is possible to conserve the energy normally emitted as light; for instance, if one of these derivatives is illuminated in liquid air it can be rubbed at that temperature without becoming luminous. When it is warmed, however, the luminescence appears. Light also induces certain reactions of the siloxens; for instance, organic halogen compounds of various kinds, *e.g.* bromoform and carbon tetrachloride, react only in the light as follows :

$$\equiv SiH + RX \longrightarrow \equiv SiX + RH.$$
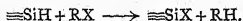
With other reagents further photochemical reactions can be obtained; thus a mixture in alcohol of siloxen, ethyl iodide and water evolves methane vigorously when illuminated and a dark red oxysiloxen is obtained. A mixture of siloxen, bromoform and water is so sensitive to light that the striking of a match is enough to produce a reddening of the white surface of the siloxen. Purely chemical influences can produce active centres in the siloxen crystals even in the dark; thus traces of oxygen suffice to start up a vigorous reaction with bromoform. Many more molecules of the silicon compound are activated by the light than actually take part in the chemical reaction, and they then emit the absorbed energy as light of a different wave-length, *i.e.* they fluoresce. When the energy is derived from neighbouring reacting molecules the phenomenon of chemiluminescence appears. Fluorescent dye-stuffs adsorbed on to the surface of the siloxen become brightly luminous when reactions take place.

The investigation of the siloxens is of special importance for the increase of our knowledge of surface phenomena, as they are, so to speak, all surface.

Many of the forms of silicon described in the older literature are siloxens containing hydroxide impurities.

COMPOUNDS OF BORON AND OXYGEN

Boron Trioxide and Boric Acid.—While the other compounds of boron resemble those of silicon to a great extent, the oxy-compounds are often very different. Boric acid has not the colloidal nature of silicic acid, but is well crystallised in the hydrated form and it differs from carbonic acid in forming hydrates. A hypoboric acid, BH_3OH, is also known which has no equivalent among the acids of silicon. A separate discussion of the compounds of boron and oxygen is therefore necessary.

Only the trioxide of boron, B_2O_3, is well known, but some sub-oxides have been described, the most definite of which are B_2O_2 and B_4O_5 (see p. 841). B_2O_3 is formed when elementary boron is burnt, but is most conveniently obtained by the dehydration of boric acid by strong heating. It melts at about 1300° and volatilises undecomposed several hundred degrees higher. It does not crystallise on cooling, but solidifies to a clear and very hard glass. The fused oxide, however, is quite a limpid liquid compared with molten silica. It takes up water very quickly from the air. Hydrates with $\frac{1}{2}$, 1 and 3 mols. of water are known, giving the acids

$H_2B_4O_7$	HBO_2	H_3BO_3,
Tetraboric acid.	Metaboric acid.	Orthoboric acid.
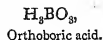
and possibly a higher hydrate of the latter which is stable below 0°. Di- and tri-boric acids are known in the form of their salts. Ortho-boric acid is stable up to about 70°. Metaboric acid is formed from it at 100°, and tetraboric acid at 140°. Boric acid, when dehydrated to a definite stage, is distinguished by very strong phosphorescence after exposure to light, a phenomenon which is connected with the presence of certain organic impurities which cannot be removed by recrystallisation.

Boric acid is soluble in water only to the extent of about 5 per cent. at 25°, but is very easily soluble in hot water. It is obtained from the naturally occurring free boric acid in fumaroles, by taking advantage of the volatility of boric acid in water vapour; or natural borates are decomposed by heating with acids, when boric acid crystallises out on cooling in white, pearly, flexible, hexagonal scales. Instead of using acids the borates may be treated with chlorine, since they are easily hydrolysed, and the metallic hydroxide thereby formed is converted into chloride and chlorate by the chlorine. Or they may be boiled with ammonium chloride, when the chloride of the metal and free ammonia are produced, while the boric acid crystallises out on cooling. The hydrolysis of the borates is due to the fact that boric acid is not a strong acid, being scarcely stronger than hydrocyanic acid, while it is much weaker than hydrogen sulphide or carbonic acid. It is, however,

considerably stronger than silicic acid, and its sodium salt is only 0·84 per cent. hydrolysed in 0·1 N NaBO$_2$ solution, while borax, Na$_2$B$_4$O$_7$, in similar concentration is hydrolysed only 0·3 per cent., since in the aqueous solution of this substance there is more free boric acid, which represses the hydrolysis of the remaining salt. These salts are always alkaline to litmus. Borates are precipitated very easily from the salts of heavy metals, and on account of this hydrolysis are mixed with hydroxides. As in the carbonates (p. 802), a heavy metal borate can be formed from solutions only if it is less soluble than the heavy metal hydroxide, which happens with the lead and silver salts. If the metal hydroxides are fairly soluble (alkalis, alkaline earths, thallium and magnesium) the preparation of the borates from solution by double decomposition offers no difficulty, but should there be no appreciable difference in solubility (Zn, Cu, Ca) then the borates and hydroxides separate together. As the solubility of the borate increases more rapidly with rise of temperature than that of the hydroxide, hydroxides are sometimes precipitated on heating and borates are obtained in the cold. The increased hydrolysis on heating also plays a part in this result.

The borates precipitated by double decomposition are never the normal salts, since the dissociation of the very weak boric acid, H$_3$BO$_3$, tends at the most to give one hydrogen ion. Normal salts can be obtained only from the fused mass. The borate which is precipitated from solution is derived from ortho-, meta-, or tetra-boric acid in a way which cannot be anticipated, and in fact all three types are obtained by precipitation, e.g.: AgBO$_2$; Ca(H$_2$BO$_3$)$_2$; Na$_2$B$_4$O$_7$. Hence all kinds of ions which can be formed from boric acid are present in solutions of boric acid and of its salts. Hydration in this case is no slow process, as in the phosphoric acids which are low in water content, but takes place instantaneously, as in the arsenic acids (cf. p. 732). For this reason a solution of Na$_3$BO$_3$ which has been made from the salt and water is completely identical with one obtained by treating NaBO$_2$ or Na$_2$B$_4$O$_7$ solution with the corresponding quantity of caustic soda; this may be confirmed by freezing-point determinations or by finding the distribution coefficient. In amyl alcohol boric acid dissolves only in its unimolecular form, and if such a solution of boric acid is shaken with an aqueous solution of a polyborate, the concentration necessary for it to remain unaffected by the aqueous solution may easily be found; from this the quantity of simple boric acid molecules contained in the latter can be determined.

Boric acid not only forms complex compounds with itself, but also with other acids, mainly those of the fifth and sixth group metals, and thus resembles silicic acid. Boro-tungstic and -molybdic acids are known, which correspond exactly to the silico-tungstic acids (cf. p. 500 et seq.). The formation of complex compounds of boric acid with

organic hydroxyl compounds is very characteristic. It is therefore easily soluble in alcohols, even in the higher ones, and forms addition compounds with all kinds of hydroxy-acids, which can be used for the quantitative estimation of the latter. Boro-tartaric or -malic acids have a characteristic power of rotating polarised light, and the amount of boric acid present may be determined from the change in the rotation caused in free tartaric or malic acid, when an unknown quantity of boric acid has been added.

Numerous formulae are given for the various borates. Those derived from the following acids will be described:

$$H_3BO_3 \qquad H_2B_2O_4 \qquad H_2B_4O_7 \qquad H_2B_6O_{10}$$
$$H_2B_8O_{13} \qquad H_2B_{12}O_{19} \qquad H_6B_4O_9 \qquad H_8B_8O_{15}$$
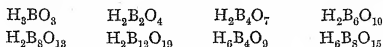
Naturally-occurring boracite, $Mg_7B_{16}O_{30}Cl_2$, is a derivative of the last acid in the list. All these types are not found in the salts of all metals; most of the series of alkali salts have the formula $M_2O \cdot mB_2O_3$, in which m has the values 1 to 4 (in potassium up to 6). In ammonium borate m can be only 2 or 4.

The borates obtained from aqueous solutions usually contain water of crystallisation. Those of the heavy alkalis are very easily soluble, those of the light alkalis still fairly soluble, and those of the alkaline earths soluble with difficulty. Alkali borates always crystallise with water of crystallisation, and $NaBO_2$ can also have methyl alcohol of crystallisation. The best known salt is borax, $Na_2B_4O_7 \cdot 10H_2O$; it crystallises readily, being easily soluble on warming, but not very soluble in the cold; it is also easy to prepare. One hundred parts of water dissolve:

Temp.	10°	50°	100°
	1·6	10·6	52·5 parts of borax.

Above 60° it crystallises in octahedra (not regular) with 5 mols. water, below this temperature as "prismatic" borax with 10 mols. water, which effloresces in dry air. In the presence of sodium chloride the transition point is depressed to 35·5°. The salt may be obtained by melting sodium carbonate and boric acid together, since this acid can drive off the stronger carbonic acid and even stronger acids on heating, as it is less volatile. Prepared in this way it forms anhydrous "borax glass," which melts at 875°. Borax and the alkali borates in general are completely volatile when heated strongly, and leave no residue.

Various borates can be obtained by melting boric acid with metallic oxides, depending on the quantity of the metallic oxide used. Calcium oxide, for example, forms three compounds with boric acid, as may be confirmed by the fusion curves: $CaO \cdot B_2O_3$, $CaO \cdot 2B_2O_3$ and $2CaO \cdot B_2O_3$. All oxides do not behave in the same way towards fused boric acid and B_2O_3 respectively, and four types may be distinguished.[1]

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[1] Gürtler, *Z. anorg. Chem.*, 1904, 40, 225.

I. Those oxides which dissolve very little in B_2O_3 or not at all. Among these are the dioxides of Si, Zr, Th, Mo, U, W and Sn, and also BeO, Al_2O_3, Cr_2O_3, Y_2O_3 and Er_2O_3.

II. Those which give completely clear, homogeneous melts. These are the oxides of the alkali metals, thallium and silver. These melts solidify on cooling to clear glasses when they have a high B_2O_3 content, but crystallise when the content of metallic oxide is high.

III. Those which give clear melts at high temperatures, but which disintegrate on cooling and form an emulsion. These are Cu_2O, PbO, Bi_2O_3, As_2O_3, TiO_2, MoO_3 and WO_3.

IV. Those which are not miscible with B_2O_3 in all proportions, even on heating. The melt therefore has two layers—the upper one, which, in the presence of an excess of B_2O_3, consists of almost pure B_2O_3, while the lower metallic borate does not usually have a very acid composition. The oxides of many bivalent metals are in this class: those of the alkaline earths, magnesium, Zn, Cd, Mn, Fe, Co, Ni, and also those of the rare earth metals Ce, La, Pr, Sa, Gd.

The form and size of the groups (BO_3) and (CO_3) is much the same, and the borates of tervalent metals are sometimes isomorphous with the carbonates of bivalent metals. In the latter there is the calcite type with ionic radius between 0.78 and 1.06 Å and the aragonite type with the larger ions of 1.43 Å radius. Actually, it is found that tervalent metals of small radius (Sc, In) give borate crystals of the calcspar type, while those of greater radius (La) give the aragonite form.[1]

Hypoborates and other Lower Acids and Oxides of Boron.—

The hypoborates, the potassium and sodium salts of which are known in the solid condition, while those of the alkaline earths exist in solution, are formed by the action of B_2H_6, or better of B_4H_{10}, on alkalis. If a stick of potassium hydroxide is kept in an atmosphere of B_4H_{10} it becomes covered with a white fur of the crystallised hypoborate, hydrogen being evolved at the same time :

$$B_4H_{10} + 4KOH \longrightarrow 4KOBH_3 + H_2.$$

This salt is stable when dry.[2] If B_4H_{10} (slightly soluble in pure water) is digested with a solution of an alkali hydroxide it is quickly dissolved according to the above equation. From B_2H_6 and solid KOH the same salt is formed, but if water is present B_2H_6 is very rapidly hydrolysed to boric acid and hydrogen. There is thus a close relationship between the boranes and hypoboric acid.

Potassium hypoborate exists in two isomeric forms[3] and conductivity measurements have shown that the doubled formula is correct $(K_2O_2B_2H_4)$. The formulae are probably those of cis- and trans-forms, viz. :

$$\begin{bmatrix} H \cdots B \cdots OH \\ \vdots \\ H \cdots B \cdots OH \end{bmatrix}^- H^+ \quad \text{and} \quad \begin{bmatrix} H \cdots B \cdots OH \\ \vdots \\ OH \cdots B \cdots H \end{bmatrix}^- H^+$$

α-Compound.   β-Compound.
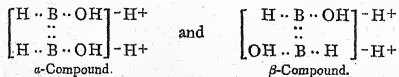
The α-compound can readily lose 4 hydrogen atoms of acidification :

[1] Goldschmidt, *Göttinger Nachr.*, 1932, 53.
[2] Stock and Kuss, *Ber.* 1914, 47, 810.
[3] Ray, *Trans. Faraday Soc.*, 1937, 33, 1260

$H_4B_2(OK)_2 + 2H_2SO_4 \longrightarrow 2KHSO_4 + B_2(OH)_2 + 2H_2$. With iodine[ ] the resulting solution gives: $B_2(OH)_2 + I_2 \longrightarrow B_2O_2 + 2HI$. The β-compound forms a tetra-potassium salt 'with alkali, $K_4H_2B_2O_2$. Solutions of potassium hypoborate are not very stable, especially when they contain only a little free alkali.

Unimolecular hypoboric acid is comparable with hypophosphorous acid:

$$\left[P{O_2 \atop H_2}\right]H \qquad\qquad \left[B{O \atop H_3}\right]H,$$

but is more unstable and therefore a stronger reducing agent. Thus it immediately precipitates copper (hydride) from copper sulphate solutions, and the free metals from solutions of Ag, Hg, Bi, Sb and As salts, but black insoluble nickel boride, Ni_2B, from nickel solutions. With nitric acid a very stable yellow to brownish red colour soon appears; if the solution is evaporated and the residue taken up with water the coloured substance goes into solution again. Finally, when potassium hypoborate is heated, a portion of the potassium distils off at $500°$ in the metallic form.

In the preparation of the boron hydrides Mg_3B_2 is hydrolysed with acid; if the hydrolysis is carried out using water, hydrogen is evolved. On extraction of the solid residue with ammonia, a compound of the formula $H_{12}B_4O_9$, "boron hydrate," is obtained, which when heated yields $H_2B_4O_6$. This compound, which may be prepared also by heating excess magnesium with B_2O_3 and acidifying the product, may be de-hydrated by gentle heating, with the formation of B_4O_5. It is interesting that all the stages from $H_{12}B_4O_9$ to B_4O_5, except the last, consist of dehydrogenation.

B_2O_2, while not actually isolated, is known to exist in the form of its acid, $B_2(OH)_4$ and some esters, e.g. $B_2(OCH_3)_4$. It is believed to be formed in the hydrolysis of B_2Cl_4,

$$B_2Cl_4 + 2H_2O = B_2O_2 + 2HCl,$$
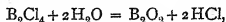
since in this reaction no hydrogen is evolved. This oxide is also formed from hypoborates (above). $B_2(OH)_4$ is a white solid, soluble in water and is a powerful reducing agent.

All the lower boric acids can be regarded as derived from B_4H_{10} by hydrolysis, though this reaction has only been carried out experimentally for $B_2H_6(OH)_2$, the least stable of them.

THE PER-ACIDS OF THE FOURTH GROUP AND OF BORON

Boron, carbon, germanium, titanium, zirconium and thorium form per-compounds similar to persulphuric acid and to Caro's acid (p. 590). The resemblance is greatest in the percarbonates, which will therefore be discussed first.

In the *percarbonates*, as in the sulphur compounds, two forms are distinguishable: those in which one hydroxyl group of the carbonic acid is replaced by $-O.OH$ (corresponding to Caro's acid), and those in which two CO_2H residues are united by a bridge of two oxygen atoms (corresponding to per-disulphuric acid). The latter are formed, like the persulphates, by electrolytic oxidation:

$$\begin{array}{ccc} \overset{OM}{\underset{O}{CO}} \quad \overset{MO}{\underset{O}{CO}} & \longrightarrow & \overset{OM}{\underset{O}{CO}} \quad \overset{MO}{\underset{O}{CO}} \\ O + O & & O \underline{\quad\quad} O \end{array}$$
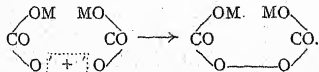
The anode potential must be made as high as possible, which is facilitated by using a neutral solution; the concentration and current density should also be as high as possible, and the temperature low ($-10°$). The preparation of percarbonates is somewhat more difficult than that of the persulphates, as they are more easily decomposed. The sodium and ammonium salts have been prepared in solution in this way, but the sky-blue (?) potassium salt and the white rubidium salt have been obtained in the solid condition.[1] The salts are very hygroscopic, and the acids liberated from them are immediately decomposed into H_2O_2 and CO_2. The salts themselves decompose on warming: $2K_2C_2O_6 \longrightarrow 2K_2CO_3 + 2CO_2 + O_2$.

The compounds of the other type do not have the $O.O$ grouping between two carbon atoms. The simplest derivative is $NaO.CO.OONa$. On warming they give off oxygen only, not CO_2: $2Na_2CO_4 \longrightarrow 2Na_2CO_3 + O_2$. These compounds are prepared from an alkali carbonate and hydrogen peroxide, or better, by passing gaseous carbon dioxide into a cold solution of $NaO.ONa$ or $HO.ONa$.[2] In this way different salts may be obtained:

$$\begin{array}{l} CO_2 + Na_2O_2 \longrightarrow CO:(ONa)(OONa), \\ CO_2 + NaOOH \longrightarrow CO:(ONa)(OOH), \\ CO_2 + 2NaOOH \longrightarrow CO:(OONa)_2 + H_2O. \end{array}$$
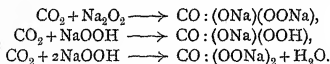
When freshly prepared these compounds contain water of crystallisation. As their aqueous solutions react almost exactly like one of H_2O_2, they are possibly ordinary carbonates which contain hydrogen peroxide of crystallisation instead of water. This is certainly true of some of them, *e.g.* the compound $K_2CO_3.3H_2O_2$, which is obtained from K_2CO_3 and 30 per cent. H_2O_2, and which can scarcely be considered as a per-compound. Most of them, however, are true per-compounds, since the water of crystallisation may be completely removed by drying, without destroying the oxidising properties. Few other salts besides the alkali compounds of percarbonic acid are known; those

[1] Constam and v. Hansen, *Z. Elektrochem.*, 1896, 3, 137.
[2] Wolffenstein and Peltner, *Ber.*, 1908, 41, 281.

prepared by double decomposition easily decompose, the silver salt being the most stable.

The tendency to formation of per-acids is appreciably less in Group IVb than in IVa. Germanium forms the well-defined per-compounds[1] $Na_3(K_2)Ge_2O_7, 4H_2O$ and $Na_2GeO_5, 4H_2O$.

The *perborates* also include compounds with hydrogen peroxide, the best known salt being $NaBO_2 . 3H_2O . H_2O_2$. It is obtained by mixing sodium borate solution with hydrogen peroxide or sodium peroxide in the cold. No salt of a true per-acid is present in it, for it does not set free any iodine from a concentrated solution of potassium iodide. The three water molecules may be driven out of the molecule by moderate heat, without changing the chemical properties of the substance. At a higher temperature *in vacuo* still more water escapes, and a yellow product remains which corresponds in its composition and properties to the formula $2NaBO_2, O_2$, but which cannot be explained as $BO_2 . ONa$, since it lacks the property of true per-acids, of liberating iodine from concentrated potassium iodide.[2] In contact with water it gives off oxygen rapidly. It is remarkable that the acidity of boric acid is considerably increased by the addition of H_2O_2. The perborates are more stable than the percarbonates, not only in the solid condition, but also in solution, from which oxygen is evolved only on warming. They are also rather insoluble, and crystallise well, especially the sodium compound, which is so slightly soluble that from a 0.5 per cent. solution of H_2O_2 at $0°$ some two-thirds of the H_2O_2 may be separated in the form of crystalline perborate. " Perborax " is completely stable in the dry condition, and is produced commercially for use in bleaching. $LiBO_3 . 2H_2O$; $LiBO_3 . H_2O$; and $KBO_3 . \frac{1}{2}H_2O$ have been isolated and perborates of other metals (Ba, Ca, Ag) may be obtained by double decomposition.

The per-compounds of titanium, zirconium and hafnium are quite analogous: $Ti\left(Zr, Hf\right)\begin{matrix}(OH)_3 \\ O . OH\end{matrix}$, and are obtained as hydrates, when solutions of the salts are precipitated with ammoniacal hydrogen peroxide. There are indications that the still unchanged OH groups may also be replaced by $-O . OH$ groups. The thorium compound has the formula $Th_2O_7 . 4H_2O$ and is not acidic, but both the others form salts, $K_4M^{IV}O_8 . 6H_2O$, of which the pertitanates are especially characterised by their intense colours. Even in acid or neutral solutions at extreme dilutions they give yellow colorations, which may be used as a test for titanium or for hydrogen peroxide. These yellow-orange salts are very stable, and may be obtained in the solid condition. Excess of hydrogen peroxide gives white compounds.

[1] R. Schwarz and H. Giese, *Ber.*, 1930, 63 B, 778.

[2] Förster, *Z. angew. Chem.*, 1921, 34, 2541.

Sulphur and Selenium Compounds of Carbon, Silicon and Boron

The sulphides of the heavier members of this group behave just like metallic sulphides (see p. 525 *et seq.*). The sulphides of boron, carbon and silicon remain to be considered. Of these carbon disulphide, CS_2, is the most interesting and important. The most prominent are those in which the fundamental elements exert their usual valency, B_2S_8, CS_2, SiS_2, but there is also a series of others (*cf.* p. 845). These ordinary sulphides are obtained by the direct union of boron, silicon or carbon with sulphur at high temperatures. In the preparation of carbon disulphide the carbon is heated electrically; at lower temperatures good yields are not obtained, since CS_2 is strongly endothermic (−25·4 Cal.), and consequently a considerable amount of heat must be supplied for its preparation. For this reason carbon disulphide shows a strong tendency to decompose at lower temperatures, and explodes on detonation. If no such impetus for decomposition is forthcoming, carbon disulphide may be kept quite safely at room temperature, but it ignites at 232° when mixed with oxygen; the flame has a remarkably low temperature (ca. 150°). In direct sunlight gradual decomposition also takes place, and the liquid is coloured yellow.

Carbon disulphide is unimolecular. It boils at 46·25°, while SiS_2 and B_2S_8 are solid compounds which are difficult to volatilise. SiS_2 forms long white silky needles; B_2S_8 a white crystalline or glassy mass which melts in the neighbourhood of 310°. Both these substances, in contrast to CS_2, burn in oxygen with difficulty. SiS_2 is slowly hydrolysed by water to silicic acid and hydrogen sulphide, and B_2S_8 is hydrolysed with violence. Carbon disulphide undergoes an obscure change with water: very pure carbon disulphide, which does not possess the unpleasant odour of the ordinary substance, but has a pleasant smell, acquires the well-known odour again when shaken with water. The odoriferous impurity, to which the colour of carbon disulphide is partly due, may again be removed by means of oxidising agents, and the substance obtained as a completely colourless liquid. The optical dispersive power of CS_2 is almost six times as great as that of flint glass. If yellow phosphorus is dissolved in it the refractive index is still higher.

Carbon disulphide is somewhat heavier than water ($d = 1·27$) and almost insoluble in it (at room temperature 0·002 vol. in 1 vol. water). It dissolves the heavier non-metals (sulphur, selenium, bromine, iodine, phosphorus) and many organic compounds very readily, but does not dissolve salts. Boron sulphide, B_2S_8, also dissolves sulphur in all proportions. It thus forms a compound B_2S_6, which is a white powder (m.pt. 390°), and in which boron may be pentavalent. There is no good solvent for boron sulphide, but PCl_8 dissolves it slightly.

Carbon disulphide corresponds to CO_2 as an acid anhydride. Just as the latter forms carbonates with bases, so CS_2 forms thiocarbonates with metallic sulphides: $CS_2 + MS_2 \longrightarrow M_2CS_8$ (*cf.* p. 811), and just

as CO_2 gives ammonium carbamate with NH_3 (p. 810), so CS_2 forms thiocarbamate $NH_2 . CS . S . (NH_4)$ with ammonia. Per-thiocarbonates of the alkalis and alkaline earths, M_2CS_4, are also known, formed from CS_2 and M_2S_2. They form yellow crystals.[1] Free thiocarbonic acid is more stable than free carbonic acid; it separates as an oily liquid when acid is added to a solution of a thiocarbonate, and decomposes only gradually into CS_2 and H_2S. Free per-thiocarbonic acid also forms an oil but is much less stable. Both acids are more stable in the presence of organic solvents than when in contact with water. Their salts are referred to on p. 811. A thioboric acid is also known in the free state, and even the acid HBS_2 corresponding to metaboric acid. This is obtained by decomposing boron bromide with hydrogen sulphide: $BBr_3 + 2H_2S \longrightarrow HBS_2 + 3HBr$; it forms white needles of melting point 120°, which give off H_2S at the ordinary temperature and are violently hydrolysed by water. In liquid ammonia they form the intensely yellow addition compound, $B_2S_3, 6NH_3$.

Selenides and Tellurides.—Selenides are known which correspond to the sulphides; those of boron and silicon, B_2Se_3 and $SiSe_2$, are obtained synthetically from the elements at a high temperature, when H_2Se may be used to advantage instead of free selenium, as it yields selenium at the working temperature. Both substances are solid, the silicon compound being iridescent, and that of boron a yellow mass which is hydrolysed by water, but is otherwise quite stable. CSe_2 (b.pt. 124°/760 mm., m.pt. −45·5°) is obtained from H_2Se and CCl_4 at 500°. Carbon telluride, CTe_2, with a garlic odour, is only known in CS_2 solution, and decomposes slowly in it at ordinary temperatures, more quickly in sunlight or at 100°; its formula may be ascertained from the quantities of tellurium and carbon which then separate. This substance is more strongly endothermic than CS_2, since it is formed only at high temperatures, *e.g.* if an arc is passed between tellurium electrodes in CS_2 vapour, or preferably, in liquid CS_2. It cannot be isolated from the solution. $CSSe$ and $CSTe$ are also obtained by striking an arc, with Se or Te anodes under CS_2.

Lower Sulphides.—Besides those compounds which correspond to the maximum valency of the elements there are sulphides in which silicon and carbon may be only bivalent. The sulphide CS and the silicide SiS correspond to carbon monoxide. Here again the silicon compound is polymerised, and is formed as yellow needles at white heat; it is solid and hydrolysed by water, whereas the carbon compound at low temperatures is probably unimolecular, and not attacked by water. It is formed by the action of a silent electric discharge on the vapour of carbon disulphide at −185°. The compound, which is solid and white at this low temperature, polymerises to a brown substance at a slightly higher temperature. The so-called carbon subsulphide, C_3S_2, which, as a result of its organic derivatives, is to be formulated as $S : C : C : C : S$, has its analogue in carbon suboxide, C_3O_2 (*cf.* p. 781). Carbon subsulphide is formed on heating carbon disulphide to a high temperature, *e.g.* by passing it through a quartz tube heated to

[1] Yeoman, *J. Chem. Soc.*, 1921, **119**, 38.

1000° or by burning an arc in it, or better, by scattering a finely divided metal (Sb) in it during the heating. Carbon subsulphide is a bright red liquid with a pungent odour; at 90° it has a vapour pressure of 48 mm., and is thus much less volatile than carbon disulphide. On further heating it polymerises to a black substance, solidifying at −0·5°. In accordance with its unsaturated condition it adds on bromine; it is soluble in benzene, carbon disulphide, etc.[1]

Oxysulphides.—Carbon and silicon also form sulphides which contain in addition oxygen or halogen. Silicon oxysulphide is only little known, but carbon oxysulphide, COS, is more stable than carbon disulphide, as it is the intermediate step between this endothermic compound and carbon dioxide. Its heat of formation is positive (37 Cals.). Carbon oxysulphide is always formed when carbon, oxygen and sulphur, or their compounds such as CO, CS_2, SO_2, are brought together at higher temperatures. The subsequent reactions are determined by the equilibria:

$$COS \rightleftharpoons CO + S \qquad and \qquad 2COS \rightleftharpoons CO_2 + CS_2.$$
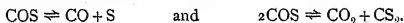
The quantities present in the equilibrium mixtures at atmospheric pressure are as follows:

Temp.		100°	200°	300°	400°	500°	600°	700°	800°	950°	
CO + S	.	—	—	—	0·5	1·5	6	16	33	64	per cent.
$CO_2 + SO_2$	.	19	27	34	39	42	43	41	33	19	,,
Unchanged COS	.	81	73	66	61	56	51	43	34	17	,,

The first of these equilibria is affected by alterations in pressure, while the second is independent of these variations; the attainment of equilibrium is very largely dependent on the presence of suitable catalysts. The CO_2 reaction proceeds rapidly in quartz or glass but not in platinum. On the other hand, the CO reaction is catalysed by platinum, though the metal is poisoned, as far as this action is concerned, by previous exposure to the vapour of carbon disulphide. Even at the ordinary temperature, carbon oxysulphide is rapidly decomposed by quartz, though it can be kept in glass vessels for years. Its formation is especially favoured by the presence of kaolin. Carbon oxysulphide may be obtained very pure and free from these impurities by heating thiocyanic acid, which may be considered as its imide, with sulphuric acid: $CSNH + H_2O \longrightarrow CSO + NH_3$, or by the decomposition of ammonium thiocarbamate with hydrochloric acid: $NH_2 . CO . SNH_4 + 2HCl \longrightarrow COS + 2NH_4Cl$. Its formation from sulphur and carbon dioxide at high temperatures allows metallic sulphides to be freed from excess sulphur by a stream of carbon dioxide at 250°, a reaction which is used in analysis.

In its physical properties carbon oxysulphide is intermediate between CO_2 and CS_2. It is a colourless, odourless gas, which con-

[1] Stock and Prätorius, *Ber.*, 1912, 45, 3568.

denses to a liquid at $-47.5°$, less soluble in water than CO_2 but more than CS_2 (about 1 volume in the cold). It burns in air with a blue flame and is explosive in a mixture with oxygen, but much less so than CS_2.

Halogeno-sulphides. — For details of the carbon compounds containing both halogen and sulphur, text-books of organic chemistry must be consulted. Of silicon the compounds $SiSCl_2$ and $SiSBr_2$ are known; they are formed at red heat from SiS_2 and halogen, or from $SiCl_4$ and H_2S. Both form colourless, long needles, which are soluble in carbon disulphide, but are decomposed by water, and give a diamide $SiS(NH_2)_2$ with liquid ammonia. The chloro-compound melts at $75°$, the bromo-compound at $93°$. A compound still richer in chlorine, $SiCl_3 . SH$, is also known. It is a colourless liquid, b.pt. $96°$, and is immediately decomposed by water.

CARBIDES, SILICIDES AND BORIDES: INTER-METALLIC COMPOUNDS

Carbides, silicides and borides—Formation of alloys—Intermetallic compounds—Thermal analysis—Compounds of metals with hydrogen—Hydrides.

Carbides, Silicides and Borides

THESE three classes of substances have in every respect a very close resemblance to one another. They are all formed by heating carbon, silicon or boron respectively, with the appropriate metal. It is not always necessary for the components to be used in the fused state, for the penetration is complete far below the melting point, *e.g.* in case-hardening iron, when the iron is embedded in carbon and heated to temperatures below its melting point, it takes up the carbon to form a carbide. Similarly, the slightly exothermic reaction between silicon and carbon takes place at 1250°, and rapidly at 1400°—still far below the melting points of the elements. The reaction temperature may be depressed if one of the components is used in solution. Thus, by the addition of another metal to a solution of silicon in molten copper, the silicide is obtained.

All metals do not unite directly with carbon, boron or silicon; it seems necessary first to form a solution of these elements in the metal; gold, bismuth, tin and perhaps the alkali metals do not dissolve carbon; others (silver, copper, platinum) dissolve it, but deposit it completely on cooling as graphite. Also, if the boiling point of the metal is reached before the reaction sets in, it is not possible to obtain carbides by direct fusion (the alkali metals, mercury and perhaps also zinc, cadmium, lead), and if there is not another method of preparing these compounds, as in the alkali carbides, they remain unknown. Finally, at very high temperatures, the carbides may be no longer stable; if, therefore, their decomposition point lies below the temperature at which the reaction can take place quickly enough, they cannot be made. The union of metals with carbon, silicon and boron is often a strongly exothermic process, so that it is sufficient to bring the mixture into reaction by means of an ignition fuse at one point, upon which the reaction proceeds throughout the entire mass. If pure carbides are desired sugar charcoal is used.

It is not, however, necessary to have carbon, boron, silicon or the metal in the elementary condition to begin with. A mixture of the oxides can be reduced when the necessary high temperature for the union to boride, silicide, etc., is attained. Carbon is heated with the metallic oxide or carbonate, which is first reduced to the metal, and then the metal combines with the excess of carbon to form a carbide.

Moissan, to whom especially we owe our knowledge of these three classes of compounds, used his electric furnace for carrying out the processes. It could be used either with the arc as a source of heat, or as a resistance furnace. In the first case the arc is struck between two electrodes of carbon, and its heat serves as a source of energy for the promotion of chemical reaction. In the second case a rod electrode and a carbon crucible serve as the poles. After the production of a small arc the reaction mixture is poured in and the current passes through it. The rod electrode is drawn out further after the mixture has become sufficiently conducting, more of the reaction mixture is poured in and so on ; the mixture conducts the electric current, thereby becoming heated, and its constituents then react with each other.

The use of boron and silicon for the formation of borides and silicides is exactly analogous. B_2O_3 may be reduced by a metal, when the boron formed immediately converts the excess metal to the boride, or metallic silicates or borates may be heated with carbon electrodes in the electric furnace, when they are reduced to silicon or boron and metal and metallic silicide or boride. The use of free silicon to reduce the metallic oxide has no advantages, since the reduction temperature lies so high that electrical energy is necessary to reach it; only the alkaline earth silicides are obtainable from the oxides of the alkaline earths and silicon at the temperature of molten iron. On the other hand, it is sometimes advantageous to use carbides rather than carbon as reducing agents ; borides, for instance, are obtained in this way by heating B_2O_3 with carbides. Metals may be used as reducing agents instead of carbon, and silicides are obtained if a mixture of metallic oxide, quartz and sodium or aluminium in coarse powder are heated together, as in the Goldschmidt process.

Other methods of preparation are only exceptionally used. Silicides and borides can be obtained by passing the vapours of compounds containing silicon or boron over the red-hot metal. Carbides are also formed by passing hydrocarbons over the heated metals and by treating solutions of metallic salts with acetylene. Some of these carbides are explosive and can be regarded as *acetylides*. If gaseous acetylene is passed into an ammoniacal solution of cuprous chloride or silver nitrate or into a solution of HgI_2 in potassium iodide or into aurous thiosulphate, precipitates of Cu_2C_2, Ag_2C_2, HgC_2, Au_2C_2 are immediately formed, which, after drying, explode on moderate rubbing, and are therefore completely different from ordinary carbides. Solutions of the alkali metals in liquid ammonia also react in a similar way with acetylene. The intensely blue-coloured liquids are decolorised when the gas is passed in, and the colourless compounds $NaHC_2$, KHC_2 are formed, which may be regarded as acid salts of acetylene. They are non-explosive, beautifully crystallised, and therefore probably true carbides ; they are also formed from undissolved alkali metals and gaseous acetylene at somewhat higher temperatures, the potassium compound at room temperature, the sodium compound only after melting the sodium. They decompose above 200°, giving off acetylene, $2KHC_2 \longrightarrow K_2C_2 + H_2C_2$, and leaving behind the normal carbides. MgC_2 is prepared by heating magnesium with acetylene.

It has been pointed out that alkali carbides, except lithium carbide, are not obtainable from the metals and carbon, since the alkali metals have too low a boiling point, and the carbides probably a low decomposition temperature. For

similar reasons the silicides and borides of the alkalis cannot be prepared by direct union; lithium silicide can be prepared direct owing to the fairly high temperature of volatilisation of lithium. It decomposes *in vacuo* at 600°. If silicon or boron hydrides are used to prepare alkali silicides or borides these substances can be obtained in every case.

The carbides, silicides and borides may be compared in their properties on the one hand with the phosphides or sulphides, and on the other hand with the compounds which the metals form with one another. The tendency of the alkaline earth and closely related compounds to hydrolyse and their colourless or saline appearance recalls the phosphides and sulphides. The non-hydrolysing compounds look metallic compared with these; they resemble intermetallic compounds in their metallic properties, their marked ability to form crystals, their conduction of electricity, their weak paramagnetism and, not least, in their formulae, in which the valency of the elements only very exceptionally corresponds to that expected from the periodic system, particularly in the borides and silicides. The types of compounds formed are no doubt dependent, as in intermetallic compounds, on the interstices in the crystal lattice of the metal, which become occupied by the atoms of boron, carbon and silicon. The following synopses give the formulae of the more important compounds.

CARBIDES

Most of the carbides of the alkalis and of the alkaline earths can be regarded as salts of acetylene in which both the hydrogen atoms are replaced by the metal. They give acetylene on hydrolysis. Their formulae are as follows:

$$Li_2C_2, \ Na_2C_2, \ K_2C_2, \ Rb_2C_2, \ Cs_2C_2; \qquad MgC_2, \ CaC_2, \ SrC_2, \ BaC_2.$$
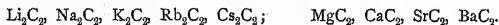
The carbides of the rare earths and of some related elements have the same empirical formulae as those of the alkaline earths; but as the rare earths are only exceptionally bivalent, and as a complex mixture of hydrocarbons is given on hydrolysis (see p. 854), these carbides cannot be looked upon as derivatives of acetylene. They are as follows:

$$CeC_2 \quad LaC_2 \quad NdC_2 \quad PrC_2 \quad SaC_2 \quad YC_2 \quad ZrC_2 \quad ThC_2 \quad MnC_2 \quad UC_2.$$
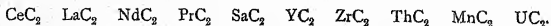
Another group may be considered as metallic derivatives of methane; aluminium and beryllium carbides give pure methane on hydrolysis, but the remainder do not hydrolyse. These compounds are:

$$Be_2C \qquad Al_4C_3; \qquad SiC \quad TiC \quad ZrC \quad HfC.$$

For others again a primary valency formula cannot, in general, be advanced, *e.g.* Cr_2C_2, Mn_3C, Fe_3C, B_6C, or only in an arbitrary manner

with the appropriate valency of the metal assumed in each instance, as, *e.g.*, in Cr_3C_2, U_2C_3, VC, NbC, TaC, Mo_2C, MoC, W_2C, WC.

SILICIDES

The formulation of the silicides and borides is still more uncertain because the products of hydrolysis are more complicated and less fully investigated. The following table gives the formulae of the known silicides:

Li_3Si	Mg_2Si	$CaSi_2$	$BaSi_2$	$SrSi_2$	$CeSi_2$	$TiSi_2$	$ZrSi_2$	$ThSi_2$
		Ca_2Si_2			$CeSi$	Ti_2Si		
VSi_2	$TaSi_2$	$MoSi_2$	WSi_2	USi_2				
V_2Si		Mo_2Si_3	W_2Si_3					
			$CoSi_2$	Ni_2Si_3 (?)				
$CrSi_2$		$FeSi_2$	$CoSi_2$	$NiSi$				
Cr_2Si_3	$MnSi$	$FeSi$	$CoSi$	Ni_3Si_2	Cu_3Si	Pt_2Si	$RuSi$	$PdSi$
Cr_2Si	Mn_2Si	Fe_3Si_2	Co_3Si_2	Ni_2Si		$PtSi$		
Cr_3Si			Co_2Si	Ni_3Si.				

It is clear that definite types of compounds are favoured, particularly those which contain one metal atom to two silicon atoms. The possibility of suitable spatial arrangement of the atoms in the crystal lattice is a determining factor in the formation of these compounds.

BORIDES

The borides show the same tendency:

CaB_6	BaB_6	Mg_3B_2	AlB_2	CrB	WB_2	Mo_3B_4
			AlB_{12}	Cr_3B_2		
MnB	Ni_3B	Co_3B	Cu_3B_2	SiB_3	CB_4	
MnB_2	NiB_2	CoB_2		SiB_6	(CB_6).	
		CoB				

It is possible that CB_6 is only an impure form of CB_4.

Physical Properties.—Carbides, silicides and borides have a pronounced tendency to crystallise, which appears when the compounds are formed from the fused or gaseous states. The silicides, in particular, build splendid crystals. The carbides of the alkalis and the alkaline earth metals are, in the pure state, colourless and transparent, *e.g.* calcium carbide, when obtained at 650° from the electrolysis of molten calcium salts with carbon electrodes. Ordinary calcium carbide, however, which is prepared by reducing lime with coke in the electric furnace, is discoloured, opaque and brittle owing to the presence of impurities. Aluminium carbide is bright yellow, with an almost golden lustre; the carbides of the more metallic elements have in contrast a colour and appearance which is not unlike that of the metal they contain,

only somewhat darker and duller. The silicides all have a metallic lustre, often like silver, even that of lithium having a dark indigo blue sheen, while those of the alkaline earths are lead to silver grey; those of the more metallic elements are altogether like metals, so that, *e.g.* ferro-silicon, which is silver white and has a beautiful metallic lustre when polished, finds a use in the preparation of articles of jewellery. Compounds very rich in silicon approach " metallic " silicon in their colour, but are more grey. Copper silicide is not reddish, but silver white, and, like many other silicides, tarnishes somewhat in air. The borides, even aluminium boride, also have a strong metallic lustre. Those of the alkaline earths and magnesium are more blackish, the crystals being brown in transmitted light. The dark flakes of boron silicide transmit yellow light. CB_4 consists of black crystals, which are very inert chemically.

The carbides, and still more the silicides and borides, are very hard very brittle, and may easily be powdered. Ferro-silicon has a maximum hardness when it contains 33 per cent. of silicon. hromium carbide scratches topaz, and niobium and tantalum carbides are used in cutting tools; the borides of the alkaline earths, of molybdenum, tungsten and aluminium scratch even the ruby, the hardest being boron carbide. Silicon carbide when condensed from the gaseous state is transparent, almost colourless, and is scarcely less hard than the diamond; it therefore finds an application as an abrasive and for drilling. The technical product (carborundum[1]) is very dark in colour, owing to impurities. It is obtained by the Acheson process in which a mixture of coke, quartz and sodium chloride, is heated by an electric arc between carbon electrodes. Calcium carbide may be employed instead of coke. As carborundum decomposes again at a high temperature into graphite and silicon, which distils (*cf.* p. 180), only graphite is found in the vicinity of the electrodes; at some distance from this crystalline carborundum is deposited, and in the outer part of the furnace amorphous silicon carbide, which can be obtained in a crystalline form by crystallisation from molten iron. Its useful physical properties may be partly explained by its structure. Analysis by Röntgen rays shows that the crystalline structure of carborundum corresponds exactly to a diamond lattice (p. 21) in which half of the C atoms are replaced by Si atoms, so that it approximates to a face-centred cubic lattice. The packing is very close, as may be expected from the great stability of the compound. The crystal lattices of the carbides TiC, VC, ZrC, NbC and TaC, however, are of the sodium chloride type (p. 299), though their constituents are neutral atoms and not ions. In cementite, Fe_3C, the iron lattice is retained and carbon occupies the interstices; cementite is, accordingly, a good conductor of electricity.

Hägg[2] has discovered some very interesting relationships between

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[1] Carborundum is a proprietary name in the U.S.A.
[2] *Z. physikal. Chem.*, 1931, B. 12, 33.

the relative sizes of the metal atoms and those of the carbon and boron atoms, by a study of the crystal structure of the carbides and the borides. He has further established a complete resemblance between the nitrides and hydrides of the metals and the corresponding carbides and borides. These compounds, or, better still, "phases," since, especially with the hydrides, it is a question of solid solutions, possess a very simple structure when the ratio of the radii of the metalloid and metal atoms has a value not exceeding 0.59. For the most part they contain close-packed cubic or hexagonal lattices of metal atoms. If the ratio exceeds this value the structure is more complex. The simple structures are "layer structures." As the number of the non-metal atoms increases, in order that the equivalent interspace between

$O = Ca$ $\bullet = C$

FIG. 72.

$O = Th$ $\bullet = C$
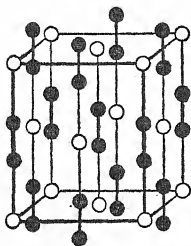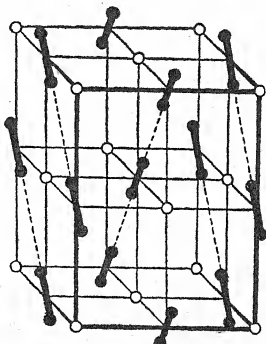
FIG. 73.

the metal atoms may be kept constant, the lattice becomes enlarged, so that the distances between the centres of the metal and the metalloid atoms increase. It can be assumed that the spheres of action of the atoms are contiguous, so that these spheres increase in size as more non-metal atoms enter. As the simple lattice is identical with that of the pure metal, one is justified in assuming that it can only expand to a limited extent. If this expansion becomes too great, a rearrangement of the lattice, with a consequent increase in the complexity of the structure, takes place.

The non-metallic atoms are arranged either singly or in pairs in the largest spaces in the metal lattice. With the arrangement of the non-metal atoms in pairs the metal lattice becomes deformed and the directions of the linked C—C varies greatly. The above diagrams

give the structures of CaC_2, and ThC_2, but the structures of Al_4C_3 and BeC_2 are much more complicated.

Most of the compounds of this class are fusible, but only at very high temperatures in the electric furnace. NbC, TaC and HfC have the highest melting points (4000°-4200°) of any chemical compounds yet measured; carborundum cannot be fused. They decompose at high temperatures in such a way that the metal distils off and the non-metal remains behind, e.g. magnesium silicide at 1100°-1200°, carborundum at 2200°. Calcium carbide decomposes at about 1810° in the presence of oxygen. The reaction $Ca + 2C \longrightarrow CaC_2$ is strongly exothermic, but the usual method of formation, $CaO + 3C \longrightarrow CO + CaC_2$, requires the addition of a large amount of heat, viz. 105·3 Cal., and as the reaction is then a system containing four phases, three solid and one gaseous, and three chemical components dependent upon each other, the system, according to the phase rule, has one degree of freedom, i.e. for every prevailing pressure there is only one temperature at which all the phases are in equilibrium. Now, since the pressure is determined by the amount of oxygen in the atmosphere, there must be an inversion point, above which the reaction proceeds from the right to the left, and below which it proceeds from left to right. This lies at about 1810°.

Chemical Behaviour.—The carbides, borides and silicides react like their individual components, but, in general, are attacked with greater difficulty. Calcium carbide burns with difficulty even in pure oxygen to form calcium oxide and carbon dioxide; carborundum undergoes only slow oxidation on heating in an oxyhydrogen blast. On the whole, only the alkaline earth compounds are attacked relatively easily; they are therefore very strong reducing agents when heated, and with their help oxides which are only reduced with difficulty yield a regulus of metal. Calcium carbide in particular is used for this purpose. Fused alkali hydroxides are the best reagents for decomposing the carbides, silicides and borides, and attack those which cannot be decomposed in any other way. The alkali hydroxide acts as a carrier of oxygen on heating, forming some alkali peroxide with the atmospheric oxygen, which then acts as an oxidising agent, and the oxides so formed give salts with the alkali hydroxide. Thus boron carbide, which is otherwise exceedingly resistant (hot fuming nitric acid does not act on it) is oxidised by molten alkali to borate and carbonate. Carborundum, which is also completely resistant to acids, is completely broken down by alkalis at red heat after some hours. Nitrates can sometimes be used for this decomposition, e.g. for calcium boride.

The borides are not usually attacked by water; and only the silicides of the alkaline earths and of lithium, and the carbides of the alkali metals, alkaline earths, beryllium, aluminium, manganese, uranium and the rare earths are decomposed by water. Dilute acids decompose some

others but many are very resistant to the attack of acids. The borides of the alkaline earths and aluminium are not decomposed by acids, but the richer the compounds are in metal the more easily acid attacks them: thus CrB is not attacked by acids, but Cr_3B_2 is attacked to some extent. MnC_2 is not dissolved, but Mn_3C, on the other hand, is easily dissolved. However, iron carbide, Fe_3C, which is exactly similar in composition, is isolated by making use of its insolubility in acids. If iron is smelted with carbon, cementated at 920°, or digested with carbon monoxide at 600°, it is permeated with a network of Fe_3C, and if it is treated with a mixture of sulphuric acid and chromic acid the unchanged iron dissolves, while the Fe_3C remains as a heavy black powder, which may be purified by boiling with fuming nitric acid. Tempered steel may contain more than 90 per cent. of its carbon as carbide, but in hardened steel only 4-5 per cent. If extracted from the latter it occasionally remains in lustrous white needles one mm. long. When dried in hydrogen it is pyrophoric and oxidises in damp air.[1]

The alkali carbides are stronger reducing agents than the other carbides. They take fire in SO_2 and in CO_2, and explode on interaction with metallic chlorides, *e.g.* lead chloride, when they give alkali chlorides. They also explode with water, decomposing into the burning metal, and carbon, which is deposited. They decompose like the carbides of alkaline earths, with the formation of acetylene, only if water vapour is passed over them slowly: $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$. This reaction, and also the reaction with bromine: $CaC_2 + 4Br_2 \longrightarrow CaBr_2 + CBr_3 \cdot CBr_3$, afford chemical evidence for the direct union of the two atoms of carbon in this carbide. All other carbides, in so far as they are decomposed by water and acids, fail to give pure acetylene. As has already been mentioned, aluminium and beryllium carbides give pure methane: $Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$. Manganese carbide gives a mixture of hydrogen and methane, although it certainly does not contain manganese in higher than the bivalent condition, since on hydrolysis it forms white manganous hydroxide. The reaction takes place to a considerable extent thus: $Mn_3C + 6H_2O \longrightarrow 3Mn(OH)_2 + CH_4 + H_2$.

The carbides of the rare earths and of uranium behave in the most complicated way on hydrolysis. The former give a mixture of gases, which consists of 70-80 per cent. acetylene, about 20 per cent. methane, some hydrogen and some ethylene. Thus ThC_2 yields on hydrolysis, 48 per cent. of acetylene, 29 per cent. of methane, 17 per cent of hydrogen and 6 per cent. of ethylene. Uranium carbide gives on hydrolysis a mixture of which one-third is gaseous and contains some 80 per cent. methane, 13 per cent. hydrogen, 5 per cent. ethylene, and only traces of acetylene; the other two-thirds is a mixture of liquid and

[1] Mylius, Förster and Schöne, *Z. anorg. Chem.*, 1904, 13, 38; *Ber.*, 1897, 29, 299.

solid hydrocarbons. The primary products of decomposition are possibly only hydrogen and acetylene or methane and the remaining products may arise from the catalytic action of the solid reactants on the gaseous mixture.

The behaviour of the silicides and borides is no simpler. Here the magnesium compounds have been largely studied, since they serve in the preparation of silanes and boranes (*cf.* p. 764). The silicide formed by the reduction: $SiO_2 + 4Mg \longrightarrow SiMg_2 + 2MgO$ gives, on hydrolysis, the whole series of silanes described on p. 766; calcium silicide, on the other hand, gives no silane on hydrolysis: $CaSi_2 + 6H_2O \longrightarrow Ca(OH)_2 + 2SiO_2 + 5H_2$.

Confirmation of Formulae. Ferrosilicon.—Owing to the similarity of many silicides and borides to alloys the recognition of the individual compounds is not easy. Metallographic methods (*cf.* p. 865) must often be applied to diagnose them as individuals. Sometimes a microscopic inspection helps to decide the formulae: thus when attempts are made to prepare a copper silicide richer in silicon than Cu_4Si, free silicon appears in microscopically visible crystals, and may be dissolved out by caustic potash, which does not attack the silicide. In most cases, however, thermal analysis is necessary. Thus in ferro-silicon, which is technically important, one might expect to find, with a content of up to 20 per cent. silicon, the compound Fe_2Si and free iron; between 20 and 30 per cent., Fe_2Si and $FeSi$; from 33–50 per cent., $FeSi$ and $FeSi_2$. The melting point, measured roughly, rises with the amount of silicon present. Exact thermochemical analysis, however, yields only the compound $FeSi$ with certainty. The alleged compound Fe_2Si probably corresponds to the approximate end-point of a series of mixed crystals which are rich in iron; alloys richer in silicon than $FeSi$, on the other hand, always contain visible crystals of free silicon, which may be dissolved out with caustic soda.

If ferrosilicon is obtained technically in the blast furnace from FeO, quartz and coke (when aluminiferous iron earths must be used instead of calcareous, or the iron goes into the slag), a product rich in iron is obtained, since at the temperature of the blast furnace the reduction of the quartz is difficult. But if it is prepared in an electric furnace ferrosilicon may be obtained with a content of silicon up to 90 per cent.

Intermetallic Compounds

Intimate mixtures of several metals are called alloys. In these important substances the metals may either be immiscible, or they may form mixed crystals or solid solutions, or actual chemical compounds may be present. The metals may be in more than one of these states in the same alloy. In spite of the numerous practical applications of alloys from the very earliest times, the theory of their production has

been studied only during the last few decades. A definition of intermetallic compounds is not easy; they have been defined as those substances in which the metallic phases of intermediate composition show evidence that electron sharing or electron transference has taken place.

In a few instances the metals or compounds in the alloy can be distinguished by the naked eye, but it is seldom possible to say without making measurements whether the metals in the alloy have undergone a change in the process of fusion. A mere chemical analysis of an alloy does not give the required information, and, in consequence, Heycock and Neville, Tammann, Roozeboom, Le Chatelier and others elaborated the method of thermal analysis (first used by Rudberg in 1830), which, in conjunction with microscopical examination, has been the chief instrument in elucidating the structure of alloys. Chemical and physical properties of the alloy throw some light on its constitution, and recently much information has been obtained from the results of X-ray analysis. Measurements of electrical conductivity, of electro-potential and of magnetic susceptibility can also be used in the detection of compounds. Even now our knowledge of alloys is still in its infancy, and few systems of more than two components have yet received detailed study. As most of the elements are metals, intermetallic compounds must form as large a class as those formed with non-metals. Their number is probably even greater, for in the former the formulae of the compounds, as already mentioned on p. 57, are largely independent of the ordinary rules of valency, and the structures assigned to such compounds are bound to have a profound influence on chemical theory. Indeed, very few of the compounds containing only two metals have formulae which have any relation to those of the salts of the constituent metals (e.g. Al_2Zn_3, $SbAg_3$, K_3Bi). Such compounds as

$$NaZn_{12}, \quad NaCd_5, \quad Cu_5Zn_8, \quad NiZn_3, \quad NiCd_4, \text{ etc.,}$$

are not paralleled in the chemistry of the non-metals. Of 150 compounds containing only metals which were catalogued by Tammann, only 35 have a composition which agrees with the valencies of the metals in them as displayed in the formation of salts. Nevertheless their formulae are all relatively simple. In binary compounds the atomic ratio 1 : 1 is common (SnAu, CoAl, NaBi) and also that of 1 : 3 ($PbPd_3$, $CaTl_3$, etc.), but other ratios are also common. There are frequently analogies in the composition of the compounds formed by the related elements, e.g.:

$$AgMg \quad AgMg_3 \quad Cu_2Zn_3 \quad Cu_2Cd_3 \quad AgCd_3 \quad Cu_3Al$$
$$AuMg \quad AuMg_3 \quad Ag_2Zn_3 \quad Ag_2Cd_3 \quad AuCd_3 \quad Ag_3Al.$$

In other series, on the other hand, there appear to be no points of

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In a few instances the metals or compounds in the alloy can be distinguished by the naked eye, but it is seldom possible to say without making measurements whether the metals in the alloy have undergone a change in the process of fusion. A mere chemical analysis of an alloy does not give the required information, and, in consequence, Heycock and Neville, Tammann, Roozeboom, Le Chatelier and others elaborated the method of thermal analysis (first used by Rudberg in 1830), which, in conjunction with microscopical examination, has been the chief instrument in elucidating the structure of alloys. Chemical and physical properties of the alloy throw some light on its constitution, and recently much information has been obtained from the results of X-ray analysis. Measurements of electrical conductivity, of electro-potential and of magnetic susceptibility can also be used in the detection of compounds. Even now our knowledge of alloys is still in its infancy, and few systems of more than two components have yet received detailed study. As most of the elements are metals, intermetallic compounds must form as large a class as those formed with non-metals. Their number is probably even greater, for in the former the formulae of the compounds, as already mentioned on p. 57, are largely independent of the ordinary rules of valency, and the structures assigned to such compounds are bound to have a profound influence on chemical theory. Indeed, very few of the compounds containing only two metals have formulae which have any relation to those of the salts of the constituent metals (*e.g.* Al_2Zn_3, $SbAg_3$, K_3Bi). Such compounds as

$$NaZn_{12}, \quad NaCd_5, \quad Cu_5Zn_3, \quad NiZn_3, \quad NiCd_5, \text{ etc.,}$$

are not paralleled in the chemistry of the non-metals. Of 150 compounds containing only metals which were catalogued by Tammann, only 35 have a composition which agrees with the valencies of the metals in them as displayed in the formation of salts. Nevertheless their formulae are all relatively simple. In binary compounds the atomic ratio 1 : 1 is common (SnAu, CoAl, NaBi) and also that of 1 : 3 ($PbPd_3$, $CaTl_3$, etc.), but other ratios are also common. There are frequently analogies in the composition of the compounds formed by the related elements, *e.g.*:

$$AgMg \quad AgMg_3 \quad Cu_5Zn_8 \quad Cu_3Cd_8 \quad AgCd_3 \quad Cu_3Al$$
$$AuMg \quad AuMg_3 \quad Ag_2Zn_3 \quad Ag_2Cd_3 \quad AuCd_3 \quad Ag_3Al.$$

In other series, on the other hand, there appear to be no points of

similarity, as, for instance, in the compounds of zinc, cadmium and mercury with sodium.

Compounds.—Compounds cannot always be detected with certainty by using only one method, *e.g.* thermal analysis and electrical resistance measurements prove the presence of LiCd, $LiCd_8$ and Li_8Cd; X-ray analysis shows the presence of the first two, but gives no evidence for Li_8Cd. Similarly, Cd_8Hg is established by X-ray analysis, but thermal and microscopical examination give no evidence for compound formation. Impurities may affect markedly the compounds formed, *e.g.* Al_7Mn and Al_8Mn have been described; small amounts of iron greatly affect the equilibria, and using very pure metals the compounds established were Al_6Mn and Al_4Mn.

The following rule of Tammann is of general application. Metals seldom combine with metals of the same group of the periodic system, and never with metals of the same sub-group; *e.g.* copper does not combine with silver, nor zinc with cadmium or mercury. None of these rules appears to be strictly true; for example, KNa_2 exists and magnesium combines with metals of both Groups IIA and IIB to form Ca_8Mg_4 and ZnMg.

A further rule gives the general behaviour of elements in different groups of the system, and applies also to non-metals: a metal either combines with all the members of a given sub-group or with none of them. There are, however, many exceptions.

Zintl[1] has shown that those elements which yield gaseous hydrides (p. 869) also give salt-like compounds with sodium dissolved in liquid ammonia, whereas the elements which are 5 to 7 places before a rare gas give metallic compounds with a simple lattice. These salt-like compounds contain complex anions, corresponding to polysulphides or polyiodides, and can be represented by the formulae:

$$Na_3[As(As)_6]; \quad Na_8[Bi(Bi)_4]; \quad Na_4[Sn(Sn)_8]; \quad Na_4[Pb(Pb)_8].$$
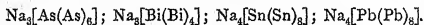
One can thus speak of polystannides and polyplumbides.

The Hume-Rothery Rules.—Three factors appear, in general, to determine the formation of intermetallic compounds—the sizes of the atoms, the crystal structure of the intermediate phases, and the ratio of valency electrons to atoms in the compound. When the atoms are of almost the same size, and where the valency electrons are unchanged in number, a wide and possibly complete range of solid solutions is formed, but no compounds, as in the system Ag-Au. When there is a great difference in size of atoms, the larger determines the crystal structure, the smaller atoms being packed into the interstices (interstitial compounds).

Between these two extremes, intermetallic compounds are found with formulae largely dependent on the relative sizes of the atoms, the same size ratio giving compounds of similar formulae, such as W_2Zr,

Bi_2K, Au_2Bi. The effect of increase in size of one atom, the valency remaining constant, is indicated by the series $LiCd_2$, $NaCd_6$, KCd_{11}.

The atoms of the second metal are accommodated by reconstruction of the crystal lattice. Thus, when zinc is added to copper (face-centred cubic lattice) the first effect is the formation of solid solutions in which the copper is displaced atom for atom and the lattice remains unaltered. When the composition approximates to CuZn, the lattice changes to body-centred cubic (β-brass). Further addition of zinc gives the γ-phase, Cu_5Zn_8, with a complex crystal structure, followed by the ϵ-phase with a hexagonal close-packed lattice ($CuZn_3$). The following relationships [1] have been found to hold in many cases :—

Phase.	Characteristics.	Examples.	Ratio of Total Valency Electrons to Total Atoms.
α	Simple solution of the two metals		
β	Body-centred cubic structure	$CuZn$, Cu_3Al Cu_5Sn, $AgCd$ $FeAl$, $CoAl$	3 : 2
γ	Cubic, large number of atoms in unit cell	Cu_5Zn_8, Cu_9Al_4 $Cu_{31}Sn_8$, Ag_5Cd_8 Fe_5Zn_{21}, Pd_5Zn_{21}	21 : 13
ϵ	Close-packed hexagonal	$CuZn_3$, Cu_3Sn $AgZn_3$, $AgCd_3$ $AuCd_3$	7 : 4

In the above types, the ratios are obtained by assuming that copper, silver and gold are univalent; zinc, cadmium and mercury are bivalent; aluminium is tervalent; and tin is quadrivalent. Group VIII metals are assumed to be zero-valent, *i.e.* as in the carbonyls (see p. 791) they do not contribute electrons in forming the compounds. It can be shown by consideration of energy levels that these ratios are a necessary consequence of atomic structure.[2] Another way of expressing the ratios is to say that the transitions

$$\alpha\text{-phase} \longrightarrow \beta\text{-phase} \longrightarrow \gamma\text{-phase} \longrightarrow \epsilon\text{-phase}$$
$$\text{occur at } 1\cdot362 \qquad 1\cdot480 \qquad 1\cdot538 \qquad 1\cdot75$$
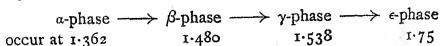
electrons per atom respectively.

Mixed Crystals.—Besides the formation of compounds in alloys, a common phenomenon is the production of mixed crystals. Liquids can mix to give a homogeneous product in which the single components can no longer be detected, and crystalline bodies can also interpenetrate in much the same way. Mixed crystals sometimes cover

[1] Hume-Rothery, *J. Inst. Metals*, 1926, **35**, 295 ; Bradley, *Phil. Mag.*, 1928 [vii], 6, 878 ; Westgren and Phragmén, *Trans. Faraday Soc.*, 1929, **25**, 379.
[2] Bernal, *Trans. Faraday Soc.*, 1929, **25**, 367 ; *Ann. Rep. Chem. Soc.*, 1935, **32**, 181; Anderson, *Chemistry and Industry*, 1937, **56**, 678.

the whole possible range of mixture from 100 per cent. of A and 0 per cent. of B to 0 per cent. of A and 100 per cent. of B; in other alloys A may dissolve only a limited quantity of B, so that outside these limits the components appear separately. The interval in which miscibility does not occur is known as the miscibility gap; the gaps in miscibility, like any other solubility-gaps, depend on temperature.

In view of the different behaviour of metals in dissolving one another the following classes must be distinguished:

1. The two metals form a continuous series of mixed crystals. Tammann has observed this property in the following pairs of metals:

Cu-Au	Ag-Au	Pb-In	Fe-Co	Ni-Co
Cu-Mn	Ag-Pd	Sb-Si	Fe-Ni	Co-Cr
Cu-Ni	Au-Pd	...	Fe-V	Ni-Pd
Cu-Pd	Au-Pt	Mn-Co	Fe-Pt	Li-Cd
Cu-Pt	Mg-Cd	Mn-Ni	Fe-Mn	...

2. The two metals form practically no mixed crystals and do not mix when molten. This behaviour is shown by the following pairs:

Ag-Fe	Ag-Co	Cd-Al	Al-Tl	Fe-Pb	Fe-Bi
K-Al	Na-Al	K-Mg	Tl-Si	Pb-Si	Bi-Cr.

3. Other sets of metals, again, mix to some extent in the liquid condition; but, on cooling, the individual components separate out. This insolubility in the solid state may even take place when the molten metals are completely miscible, and the metals may even separate on solidification even if they form mixed crystals under other conditions; e.g. at lower temperatures.

4. The metals form mixed crystals, but there is a gap in which they are non-miscible. This behaviour is found both when an actual compound is formed and also when mere solution takes place.

5. The pure metals form no mixed crystals, but the compounds which they give are able to mix freely either with each other or with one of the pure metals.

In metallographic work it is important to be able to determine the composition of the saturated mixed crystals. It is found that metals of low melting point have a greater tendency to crystallise pure from a mixture than those whose melting points are high. A high temperature usually assists the mutual penetration. The solubility of metals of low melting point in those of high melting point is usually greater than the converse.

Reaction between Metals in the Solid State.—The tendency for metals to react in the solid state is very remarkable, and is shown both in the synthetic production of compounds and of solid solutions and in their decomposition. When mixtures of powdered metals are compressed, the individual grains can be detected under the microscope, but if the mixture is warmed to a temperature below the melting point of the components, diffusion begins and the sharp edges of the grains begin to vanish. This effect can easily be seen in mixtures of tin and copper, and of copper and silver, and the fringes which form between the grains gradually spread with the heat treat-

ment. This happens whether a compound or only mixed crystals are formed; it was previously supposed that a temporary fusion took place, but it is more likely to be a diffusion process in which the atoms of one element move into the crystal lattice of the other. Self-diffusion of pure metals has been strikingly demonstrated in the case of copper and of lead, using radioactive isotopes as labelled atoms.[1] Reactions can occur, not only in coarse mixtures but also, and more easily, in solid solutions or in solid compounds. Two types of change take place.

1. Some mixed crystals disintegrate with change of temperature, because the mutual solubility of the components changes with temperature. Thus alloys of silver and tin containing 17-27 per cent. tin solidify as a whole to mixed crystals at temperatures above 490°. Below 490°, however, the solubility of silver in tin is less than corresponds to the composition of this alloy. The mixed crystals therefore decompose not into tin and silver, but into mixed crystals poorer in silver and the compound Ag_3Sn. This does not remain in a finely divided state in the solid mixture, but its molecules diffuse and unite to form visible crystals which are surrounded by the mixed crystals.

Another cause of the disintegration of mixed crystals is the conversion of one of the components at a certain temperature into another modification, in which the second metal is less soluble. This is observed in the important system iron-carbon (these effects take place in some systems not purely metallic) but is rare among alloys of two metals. Here also disintegration does not necessarily give the metallic components; in the copper-zinc system, for example, one kind of mixed crystal is converted into another.

2. A compound is decomposed into two kinds of crystals, or two kinds of crystals combine to form a compound. The latter is observed, e.g., in the system antimony-thallium. Above 195° both metals crystallise separately, but if the solid mixture is cooled to 187° they form the compound $SbTl_8$. Similarly the compound Ni_4Sn exists only below 855°, and above this temperature is decomposed into the compound Ni_3Sn, and mixed crystals which contain 15 per cent. tin and 85 per cent. nickel. Such changes are generally reversible. They are dependent on the formation of definite modifications, and become noticeable only on slowly cooling or warming the mixture, or allowing the temperature to remain constant for a long time. The microscopical examination indicates whether this thermal transition point corresponds to a structural change. As a result of the diffusibility of the atoms the crystalline form produced may often be identified with compounds obtained under other conditions.

Finally, one compound may be converted into another modification by a reversible reaction without changing its composition. Thus, for

[1] Steigman, *Phys. Rev.*, 1939, 56, 13.

example, Ag_8Al shows a transition point at 610°, CdMg at 246°, Mn_4Sn at 100°, and so on.

These decomposition and transition points may be passed over by rapid cooling. Just as the crystallisation of liquids is hindered by strong undercooling because of the increase of viscosity, so metallic systems may also be brought into a pseudo-stable state, from which they may be liberated on warming far below their transition point, when the small crystals in the glassy mass increase in size.

These properties can only be investigated with the microscope by the use of reflected light. The surfaces are etched to bring out the structure. It is necessary to use etching reagents which act slowly, and electrolytic etching, in which the metal under examination is made the anode and a feeble current passed, is also largely employed. In this way the baser portions are first attacked and the outlines of the masses of less base metal are made clear. Very often, however, mere mechanical treatment (drawing out, pressure, bending) gives obvious strain lines without chemical treatment. Alternatively, the light reflected by the polished surfaces may be analysed optically; the light is reflected unaltered from the surfaces of crystals belonging to the regular system, while from crystals belonging to other systems it is resolved into two components, which either vibrate at right angles to each other (quadratic, rhombic and hexagonal) or are elliptically polarised (mono- and tri-clinic).

Theory of Metals.—It is convenient at this point to mention the general theory of metals, which goes far to explain some of the observations in addition to the characteristic properties of pure metals. Losenty's "free electron" theory[1] depicted a metal as consisting of a close-packed arrangement of spherical metallic ions, in the spaces of which the electrons moved freely. This "electron gas" conception, however, cannot be reconciled with atomic heat observations, and has been superseded by a theory developed[2] on the grounds of the Pauli exclusion principle. More or less continuous energy levels exist for the free electrons, which, in the most stable state, occupy these levels in pairs. If this idea is accepted, a qualitative explanation of the observed temperature-independent paramagnetic susceptibility of metals is easily found. When the metal is heated, some of the pairs of electrons are broken, the unpaired electrons being transferred to levels of higher energy; the unpaired electrons contribute to the paramagnetic susceptibility of the metal, but their contribution decreases with increasing temperature, so that little actual change occurs. A satisfactory quantum-mechanical treatment of this problem has been made by Sommerfeld and others.[3] The concept of definite bands of permitted energy levels offers a theoretical explanation of the Hume-Rothery rules.

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[1] *The Theory of Electrons*, Teubner, 1916.

[2] *Zeit für Phys.*, 1927, 41, 81.

[3] See: A. H. Wilson, *Theory of Metals*, Cambridge Univ. Press, 1936; N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys*, Oxford, 1936.

The measurement of interatomic distances in metallic crystals reveals that a given atom of the metal is surrounded by two groups of atoms at two different distances. The values of these distances indicate that the conditions are satisfied for both one-electron and two-electron covalent bonds, as it is believed that resonance occurs between the many possible structures. If this is the case, then maximum stability is to be expected when maximum co-ordination number is found, which is in good agreement with the observed closest-packed arrangements in metallic crystals.

Properties.—The appearance of alloys is often very similar to that of the component metals. The crystals are frequently not perfect polyhedra but rounded in form, as the surface tension in the fused metal is large enough to overcome in part the orientating forces in the crystals. As these forces increase in power with fall in temperature more rapidly than the surface tension, the crystals which separate first are the most globular in form, while if the same constituent continues to solidify, the crystals deposited later will approximate more closely to the true shape. For example, from a copper-bismuth mixture the copper separates out in a rounded form above 800°, and in polyhedra below this temperature.

The appearance of eutectic mixtures is interesting. It might be supposed that the two components of the eutectic separated out alternately, which would then give rise to a lamellar structure; but this is not found to occur. If a eutectic mixture of any sort is allowed to crystallise, and the separation of solid is started by cooling at a point, the two components of the eutectic are deposited radially from this point. They are thus deposited simultaneously and not alternately.

The chemical properties of intermetallic compounds are often very different from those of their components; this is particularly noticeable in their resistance to corrosion. The electro-chemical behaviour of an alloy cannot be predicted from a knowledge of its components, and although a compound which contains an alkali metal cannot be expected to be very electronegative, compounds in general are often more electro-negative than either of their components. Their electrical conductivity is generally less than that of the component with highest conductivity. Some alloys are useful acid-resisting materials—particularly those which contain tantalum, tungsten, chromium and silicon. But the manufacture of these materials is at present largely conducted along purely empirical lines. The technique of the production of "rustless" iron received an impetus from the work of B. Strauss.[1] If 14 per cent. of Cr is alloyed with iron the product is passive and has a high resistance to the action of water and air, but the passivity is removed by the presence of small quantities of carbon. This trouble can, however, be overcome by the addition of nickel, which causes the carbon to remain dissolved,

[1] *Z. Elektrochem.*, 1926, **33**, 317.

with formation of homogeneous crystals of austenite. This non-tarnishing steel shows an electrochemical potential of $+0.2$ volts, while ordinary steel has one of -0.6 volts. A Be-Cu-Ag alloy (0.5-1 per cent. Be) is very resistant to the tarnishing effect of hydrogen sulphide.[1] The addition of small quantities of tellurium to lead greatly improves its resistance to corrosion and its mechanical properties. In some alloys, however, chemical reactivity is enhanced; some alloys of magnesium with lead, tin and thallium oxidise readily and completely in moist air and Na_3Sb and Na_3Bi ignite spontaneously if rubbed.

The discovery that intermetallic compounds are decomposed when an electric current is passed through them was of very great interest. Thus, when a sodium-potassium alloy is electrolysed, the potassium goes to the cathode, the sodium to the anode.[2] The alloy is thus a heteropolar compound, and the assumption of the function of a negative component by the very positive metal sodium is merely an indication that the electro-chemical properties are relative. As a rule, the sodium compound contains a much less electropositive element than sodium, with the consequence that the sodium appears at the cathode; here, in combination with the still more positive potassium, the sodium is relatively electronegative (cf. lithium hydride, p. 877).

Among the physical properties of alloys ferromagnetism has a special chemical interest. This property is shown by the alloys of iron, nickel and cobalt, metals which are ferromagnetic in the pure state. The property is lost when a certain temperature is attained, and disappears or reappears quite suddenly when this temperature is passed. The ferromagnetic property is often bound up with the existence of crystals of a particular kind, and is lost when a change in the crystal form takes place; this has been confirmed by X-ray analysis. The magnetic forms have a body-centred lattice, while the non-magnetic forms are face-centred. As this is so, it is very remarkable that the point at which the magnetic properties are lost is not very clearly brought out on the cooling or heating curves. In general, the loss of magnetic properties is not affected by other profound changes in the relations of the atom; iron or nickel retain them, at least in part, after vigorous reaction with oxygen, sulphur, phosphorus, silicon, etc. On the other hand, the magnetic properties are dependent on the valency exerted by the metal, for while FeS and Ni_3S_2 are paramagnetic, FeS_2 and NiS are not.

Some alloys of nickel and iron are not magnetic when made; on cooling them to $-100°$ they become magnetic and retain this property at ordinary temperatures, but lose it quite suddenly at about 400°. In the chrome nickel steels a small variation in the carbon content causes a profound alteration in the magnetic properties. Thus a steel con-

[1] Sloman, *Month. J. Inst. Metals*, 1934, **1**, 31.
[2] Kremann and v. Rehenburg, *Z. physikal. Chem.*, 1924, **110**, 559.

taining 20·5 per cent. Cr and 6·8 per cent. Ni, heat treated, gave 1845
magnetic units when the carbon content was 0·16 per cent., but only
17 units when it was 0·23 per cent.

Alloys of magnetic with non-magnetic metals are themselves
non-magnetic if the active metal is present only in the form of a
compound. When it is present in such quantity that mixed crystals
are also formed, so that the active metal acts as solvent for the other
or for the compound, the alloy is
magnetic. Although the magnetic
property is thus lost when a com-
pound is formed, alloys containing
mixed crystals are sometimes more
highly magnetic than the original metal
—some cobalt-chromium alloys are
one-third more magnetic than pure
cobalt. These magnetic alloys lose
this property when heated to a
particular temperature, which is lower
for the alloys than for the pure
magnetic metal.

Fig. 74.

It is very curious that some non-
magnetic metals become magnetic when
alloyed together. Thus, a manganese-copper containing 30 per cent.
Mn is itself non-magnetic, but develops pronounced ferro-magnetism
when another metal such as aluminium, zinc, arsenic, antimony or
bismuth is added to the alloy (Heusler's alloys). These alloys also
lose their magnetic properties on heating to a certain temperature.

Thermal Analysis.—The method of thermal analysis, by which the
existence of intermetallic compounds can be investigated, will now be
discussed.[1]

It often happens that when a molten homogeneous mixture of two
components is cooled one of the constituents separates first until the
point is reached when the liquid portion remaining has the com-
position of the eutectic mixture, which separates at the point at which
the solution is saturated with respect to each component. This fraction
then crystallises as a whole on further cooling. The cooling curve then
has the appearance shown in Fig. 74 above.

The line *ab* represents mere cooling of the fused mass without separation of
crystals. When the melt becomes saturated with one sort of crystal this substance
begins to crystallise out (at *b*). As this solidification takes place with liberation of
heat, the liquid does not cool so rapidly while this is going on, and consequently the
section of the curve *bc* is less steep than the portion *ab*. When enough of this
constituent has separated out to give the remaining liquid the composition of the

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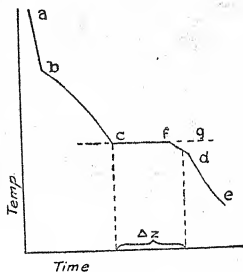
[1] The figures which illustrate this portion are taken from Tammann's *Metallo-
graphy.*

3 I

eutectic (at c), this mixture solidifies as a whole. The temperature remains constant, in just the same way as it does when water becomes ice at o°. The temperature only begins to fall again when the whole of the liquid has crystallised out. The time taken for the eutectic to crystallise out is shown by the line cg parallel to the time axis, while the further cooling of the solid is shown by the line gc. The more eutectic is present the longer is cg. The actual break at g is not usually sharply defined, owing to irregular cooling, as shown by the rounded corner fd. The point g can, however, be accurately found by finding the point of intersection of cf and ed.

If no eutectic is formed the behaviour on cooling is very similar, except that the line ab is followed immediately by a flat portion like cg, when the melt solidifies as a whole with formation of a compound.
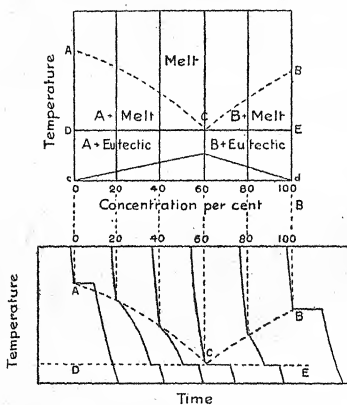
FIG. 75.

If a freezing-point diagram is now made up like that on p. 225, in which the behaviour of mixtures of different composition on cooling is indicated, the type of diagram shown above (Fig. 75) is obtained. In the lower part of the diagram the separate cooling curves are given. The composition of the eutectic is assumed to be 60 per cent. in this instance, and it can be seen that at this composition the portion of the cooling curve parallel to the time axis is longer than for any other composition. In the curves at the extreme left and the extreme right another portion becomes parallel to the time axis, owing to the crystallisation of the pure substances A or B.

The dotted line ACB joins the points in the curves where the first kink occurs, corresponding to the first appearance of crystals. This curve appears as ACB in the upper diagram as well. The space above this line in the upper diagram represents the region of existence of the fused alloy before any separation of solid has occurred. The area below DCE, in the same way, represents the completely solidified metal. The spaces ACD and BCE represent crystals of A or B in contact with the fused

mass. Immediately under C the metal solidifies to pure eutectic, while below DC a mixture of A and eutectic is formed, below CE a mixture of B and eutectic.

The time taken for the eutectic to separate out is plotted on the vertical lines in the upper diagram. Under C, where only the eutectic separates out, this is at a maximum, indicated by the peak of the triangle on *cd*. The times are plotted vertically from *cd*.

The above diagram gives, therefore, the relations of two substances which do not form either compounds or mixed crystals, and which are miscible in all proportions in the liquid state. If, now, A and B give a compound which melts at a definite temperature to a homogeneous liquid (which is by no means a general property), the accompanying diagram (Fig. 76) is obtained. It resembles that given on p. 225.

It is remarkable that the apex of the curve, which corresponds to the metal compound, is always rounded off. This is probably due to the presence of molecules of the separate metals as well as those of AB in the liquid. The greater this decomposition in the fused portion the flatter the top of the curve will be.
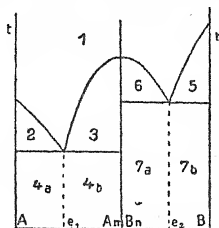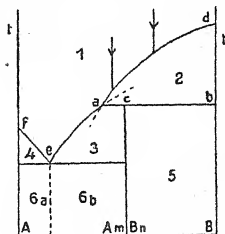
FIG. 76. FIG. 77.

In this diagram there are nine areas in all. In 1 the whole is in the molten condition. Vertically above A the pure substance A, above B the pure component B, above AmBn the compound AmBn separates out. The other parts of the diagram correspond to the following conditions.

2, A and liquid.	7a, AmBn and its eutectic with B.
5, B and liquid.	7b, B „ „ „ „ AmBn.
4b, AmBn and its eutectic with A.	3 and 6, Compound AmBn and liquid.
	4a, A and its eutectic with AmBn.

The times of crystallisation of the eutectics are represented by two maxima e_1 and e_2.

If A and B form several compounds, each compound will give a peak in the curve, and between these peaks will lie eutectic points due to the two adjacent compounds.

Very frequently the compound formed by A and B does not melt to a homogeneous liquid, but decomposes at its melting point into two parts, of which one forms the liquid phase, while the other is solid and has a higher melting point than that at which the decomposition takes place. The solidification then proceeds as indicated in Fig. 77.

Here there is no maximum in the curve above the point representing the composition AmBn. This compound no longer has a definite melting point, and the crystallisation curve which starts at the point *d* above B passes the melting point of AmBn, and then meets at *a* the curve of the eutectic between A and AmBn.

The left-hand lower corner of the area 2 thus represents crystals of B in contact with a melt richer in A than the compound AmBn. If this liquid is slowly cooled,

so that it stays for a long time between c and the dotted line above that point, the crystals of B are converted into AmBn. This change can also take place after the mass has solidified, as the atoms can diffuse even in the solid state (p. 860). Under the microscope the rapidly-cooled alloy shows crystals of B in a matrix of AB, the A crystallising as a eutectic with the rest of AmBn. When the mixture is slowly cooled no crystals of B appear.

When the mixture contains less A than corresponds to the formula AmBn and is slowly cooled, the duration of the eutectic crystallisation is similarly zero after the point AmBn is reached. In this way the assumption of the existence of the compound AmBn can be confirmed; this compound is not indicated by a maximum in the crystallisation curve, but is seen as a minimum on the curve representing the time of crystallisation of the eutectic.

There are four other ways in which the crystallisation of the liquid alloy can take place.

As in the first example previously described, A and B may form neither compound nor mixed crystals, but they may be partially soluble in one another in the liquid state. Owing to the gap in miscibility two layers will be formed when the components are fused together. The solidifying temperature of such a mixture is independent of the actual mass of the two layers, for the separation of one kind of crystal only results in the decrease in quantity of the layer from which it separates out without any alteration in the melting point.

A further possibility is the formation of a compound which gives two liquid layers in the fused state. Examples of this behaviour are rare—it is found, for example, in the compound $NaZn_{13}$.

A much commoner property is the formation of solutions in all proportions of A and B both in the solid and liquid state, without the production of a definite chemical compound. There is then no discontinuity in the curve as no eutectic exists, mixed crystals being deposited as the melt cools. The solidification curve is then more or less bent in a single line from the melting point of A to the melting point of B; the curve may be either concave or convex with respect to the composition axis. The mixed crystals can thus have either a higher or a lower melting point than that of the single components, but although the curve shows maximum and minimum values for the melting point it is smooth throughout and there are no breaks.

Finally, it sometimes happens that A and B are miscible in all proportions in the liquid state but not in the solid, or only up to a certain point. Under these conditions there is a gap in the miscibility in the crystals but two layers are not formed in the fused mass. For details of these systems text-books of metallography should be consulted.

Under the microscope the appearance of the various stages of the crystallisation process is roughly as follows. When there is a change in direction of the curve at a maximum point a conglomerate of crystals of the same sort is deposited, indicating that a single chemical substance is crystallising out; when the curve changes direction at a minimum point the eutectic is seen as small crystals of two kinds, but all of the same size. Crystallisation between maximum and minimum points also gives crystals of different kinds, but unlike those of the eutectic they are also of different sizes; they are deposited in layers, the inner layer being richer in the substance deposited at the higher temperature. Prolonged heating of the metal makes the crystals more homogeneous, owing to the diffusion of the atoms of the metal.

The Metals and Hydrogen

Hydrogen is comparable with the metals in many respects, so that some of the products of the reactions between hydrogen and metals may be included in the alloys. There are, however, at least four different types of hydrogen-metal compounds, and only one of these has the character of an alloy. These four kinds are:

1. *Gaseous Compounds.*—According to Paneth[1] all elements which occupy the 1-4 positions before an inert gas in the periodic system, and also boron, form gaseous hydrides, as shown in the following list:

III.	IV.	V.	VI.	VII.
B	C	N	O	F
...	Si	P	S	Cl
...	Ge	As	Se	Br
...	Sn	Sb	Te	I
...	Pb	Bi	Po	...

Among them are elements which are entirely or mostly metallic, such as germanium, tin, lead, arsenic, antimony, bismuth and polonium.

2. *Compounds which are like Alloys.*—Many of the heavy metals give these compounds, but not all of them. They are mainly interstitial compounds.

3. *Field Valency Compounds.*—Formed between hydrogen or very finely divided iron or nickel. Some of the compounds in Class 2 are probably also of this type.

4. *Saline Compounds.*—The metals of the first, second and third chief sub-groups of the periodic system give solid, colourless hydrides, viz. all the alkali metals, the elements calcium, strontium and barium of the second group, and the rare earths of the third group. These compounds are considered on p. 877.

Gaseous Hydrides.—Many gaseous hydrides have already been considered (pp. 606, 763). Paneth and Rabinowitsch[2] have noted some interesting comparisons between those of the metals with those of the non-metals. There is also a definite connection between many of their properties and those of the inert gases (*cf.* p. 41) which has permitted the boiling points of hydrides which have not yet been prepared in sufficient quantity, to be extrapolated—*e.g.* PbH$_4$, $-13°$; BiH$_3$, $+22°$; PoH$_2$, $+37°$. The conception of the hydride as the most volatile halide is confirmed, as will be clear from the curves in Fig. 78.

The hydrides, like the halides, are non-polar compounds with an outer electron layer like that of an inert gas, those of elements of the fourth group developing this feature to the greatest extent. In the

[1] *Ber.*, 1920, **53**, 1710.   [2] *Ber.*, 1925, **58**, 1138.

table below it can be seen that the hydrides of the fourth group are nearest to the inert gases in boiling point; after them come the mono-, then the tri-, and finally the di-hydrides with the highest boiling points. In general, the melting and boiling points become higher in each group
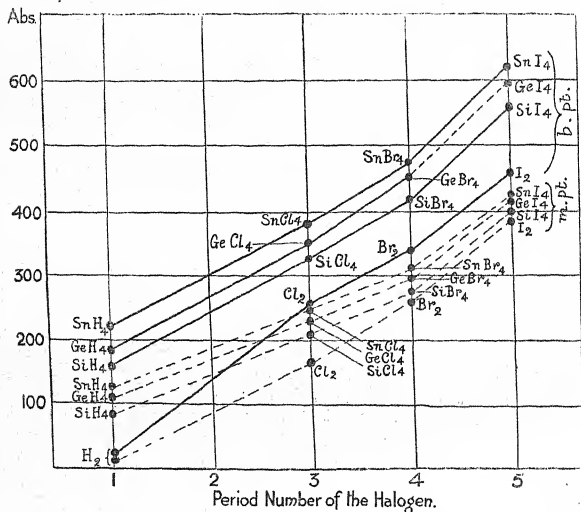
FIG. 78.—Melting points and boiling points of hydrides and halides.

with increasing period number—the rise is linear in a first approximation. The associated hydrides, NH_3, OH_2, FH, are exceptions to this rule.

Melting and Boiling Points of the Volatile Hydrides (° Abs.)

CH_4	$89°$	NH_3	$196°$	OH_2	$273°$	FH	$181°$
	$111.7°$		$239.8°$		$373°$		$292.5°$
SiH_4	$88°$	PH_3	$140°$	SH_2	$190°$	ClH	$161.5°$
	$161°$		$185.9°$		$212.5°$		$188°$
GeH_4	$108°$	AsH_3	$158°$	SeH_2	$207°$	BrH	$186°$
	$184.5°$		$218°$		$231.5°$		$205°$
SnH_4	$123°$	SbH_3	$185°$	TeH_2	$225°$	IH	$222°$
	$221°$		$256°$		$273.5°$		$237°$

The properties of the hydrides of formula MH_4 show a similarity with the next following inert gas which extends even to their molecular

volumes. According to H. Grimm[1] this is due to the equality in the total nuclear charge, for the charge on the nucleus of the central atom plus those on the four hydrogen atoms is equal to that on the nucleus of the next inert gas. The marked similarity between the $NH_4{}^{\cdot}$ ion and the $Rb^{\cdot}$ ion is due not only to the equality in the number of outer electrons but also to the equality of volume. As may be seen from the following table, the atoms which lie four or less places before an inert gas can alter their properties by taking up $a = 1, 2, 3,$ or 4

Hydrogen atoms	IV	V	VI	VII	O	I	Group
0	C	N	O	F	Ne	Na	Radius
1		CH	NH	OH	FH		
2			CH_2	NH_2	OH_2	FH_2	
3				CH_3	NH_3	OH_3	
4					CH_4	NH_4	
Valency	−4	−3	−2	−1	0	+1	

←————————————————————— Radius

hydrogen atoms. The "pseudo-atoms" thus formed are similar in properties to the real atoms which are a groups to the right of the parent atom. Hence, as the table is arranged, similar atoms and pseudo-atoms fall in the same group, e.g. OH, NH_2, CH_3 in the halogen group, HF, H_2O, H_3N and CH_4 in the inert gas group.

Alloys of Hydrogen with Metals.—The metals which take up hydrogen to form an alloy may be divided into two groups: those in which the formation of compounds with hydrogen at constant pressure increases with rise in temperature, and those in which it decreases. Iron, copper, nickel and platinum belong to the first group, palladium and tantalum to the latter. These elements absorb hydrogen when they are kept in the gas. Cd, Tl, Zn, Pb, Bi, Sn, Sb, Au, Ag, Rh are not able to do this and tungsten absorbs very little hydrogen,[2] but these metals seem to be able to form an alloy under certain conditions; thus a

[1] Z. Elektrochem., 1925, 31, 474.
[2] Sieverts, Z. Elektrochem., 1910, 16, 707; Ber., 1911, 44, 2394; 1912, 45, 221; Z. physikal. Chem., 1911, 77, 591.

lead sheet becomes roughened when used as a cathode in electrolysis. These alloys all have a metallic appearance, and the hydrogen in them plays the part of a metal. It can be proved that it is present in them in the monatomic condition, and its increased solubility with rise in temperature depends on this. The free hydrogen atoms alone are generally absorbed; they are present in some quantity in hydrogen gas at higher temperatures, and are then taken up by the metal in a definite distribution ratio. The hydrogen in these alloys precipitates noble metals from solution. There are reasons for assuming that hydrogen is also dissolved in the monatomic condition in molten metals.

Absorption of Hydrogen with Change in Pressure.—The solubility of hydrogen in solid and in liquid metals at constant temperature is proportional to the square root of the pressure of the gas. This rule is generally valid for metal-gas solutions (*e.g.* of N_2, SO_2) and is only incorrect at low pressures.

Absorption of Hydrogen with Change in Temperature.—When metals absorb hydrogen in increasing quantity with rise in temperature the increase in the absorption with temperature is almost linear, and continues up to the melting point. Here a sudden increase in solubility takes place, and on further heating the solubility increases, again as almost a linear function. If these solutions are cooled they spurt on solidification, owing to the evolution of the dissolved gas.

The course of the solubility curve may be seen from the following example, giving the quantities of hydrogen absorbed by 100 g. iron :

Temp.	409°	775°	1033°	1450°	m.pt.	1650°	
Solid	0·035	0·201	0·526	1·079	1·2	...	mg. H_2
Liquid	...	...	...	...	2·4	2·79	mg. H_2

The absorption is less in platinum ; and on cooling it is reduced almost to zero.

As an example of decrease in solubility with rising temperature some data are given for tantalum :

Temp.	17°	263°	530°	730°	1030°	1330°	
100 g. Ta dissolves	420	327	107	33·4	11·9	6·7	mg. H_2

Palladium absorbs by far the greatest quantity of hydrogen. Electrolytically deposited iron also contains more than 100 times its volume of hydrogen. Many metals are able to absorb considerable quantities of hydrogen when they are precipitated from solution, but lose this property if they are afterwards fritted—rhodium gives an example of this behaviour, in which surface absorption plays a great part. The absorption of hydrogen by copper when it is precipitated by hypophosphites is well known. The reddish deposit so formed is thought by many chemists to be a true hydride of copper ; it easily gives off the greater part of the hydrogen. In the taking

up of hydrogen by metals at higher temperatures adsorption is of little or no significance, for the gas is taken up independently of the surface area, and in proportion to the total volume of the metal; the hydrogen penetrates into the innermost portions of it. This is the cause of the marked permeability for hydrogen shown by iron or other metal tubes at higher temperatures. The alloy is formed inside the tube, but decomposes on the outside, where the pressure of hydrogen is nil. Many metals are structurally changed on heating in hydrogen on account of the alternate formation and decomposition of alloys; e.g. tantalum wires become brittle and crystalline, and even platinum itself becomes mechanically weakened if it is used as a cathode for some time. As long as the metal contains an appreciable quantity of hydrogen its physical properties are different from those of the pure metal. The volume is greater, the resistance of tantalum wire is higher than that of tantalum free from hydrogen, and the alloys have less mechanical rigidity and fall to pieces more easily. Naturally, the electro-chemical potential of metals also changes when they are saturated with hydrogen, and supersaturation with hydrogen probably gives rise to the phenomena of over-voltage in electrolysis. The varying stability of the different kinds of hydrogen alloys is one of the causes of the differences in the rate at which hydrogen is evolved at cathodes of various metals. The metal is able to take up more hydrogen while a current is being passed than it can if kept in the gas; a palladium cathode saturated with hydrogen evolves the gas for a long time after the current is switched off, when the reaction $2H \longrightarrow H_2$ takes place, for it is mainly the atomic hydrogen which remains dissolved in the metal. The absorption of hydrogen is so rapid that at the beginning no gas is evolved at a palladium cathode.

The alloy of palladium and hydrogen has received most attention as it is the richest in hydrogen of all the metallic alloys. The absorption is so considerable that thin palladium foil sags a great deal when used as a cathode for the evolution of hydrogen, since the absorption and the consequent change in volume take place almost entirely on one side. The quantity of hydrogen absorbed by the palladium depends on the form of the metal and the method of preparation of the alloy. The solid solutions obtained electrolytically from the finely divided metal are richest in hydrogen and contain almost 1000 volumes of hydrogen per volume of palladium. This is much more hydrogen than palladium is able to absorb from the gas without the assistance of the electric current. If the current is interrupted a part of the hydrogen is given up violently for some time after. The hydrogen in the alloy acts as a strong reducing agent, e.g. it precipitates mercury from its salts, and gives hydrochloric acid from chlorine water. The alloy sometimes becomes suddenly heated when exposed to the air.

This alloy was spoken of as "palladium hydride." Graham con-

sidered that "palladium hydride" was a solution, and Hoitsema[1] assumed that there were two non-miscible solid solutions; according to his view the hydrogen dissolves in the atomic condition at low pressure, and as molecules at higher pressure. According to the views of other investigators a combination of ad- and ab-sorption takes place. The solubility of hydrogen in palladium under atmospheric pressure between 600° and 1541° (the melting point of palladium) is almost independent of the temperature; at the melting point it sinks to a half of this amount.
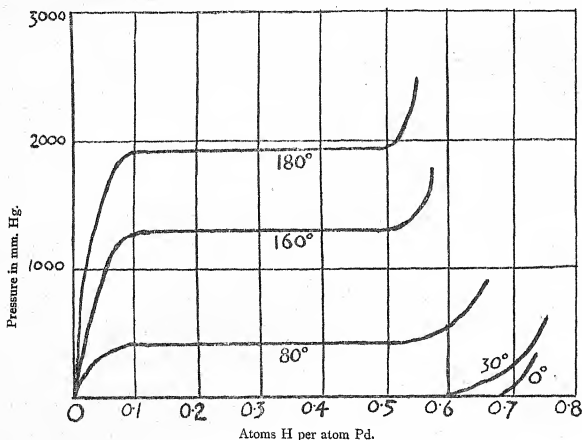
FIG. 79.

The system Pd-H has been examined with greater care by other workers, notably by Gillespie and Hall.[2] Their results are shown in Fig. 79, and show strictly horizontal portions in the regions of slight slope observed by other investigators. These were obtained by using specially purified finely divided palladium and by ensuring that true positions of equilibrium were reached. The authors consider that the results show the existence of two immiscible solid solutions. The one richer in hydrogen is very close to Pd_4H_3 or Pd_2H, which they regard as a true compound; it is obtained nearly pure at the higher temperatures, sharp breaks in the directions of the curves taking place at the composition Pd_2H, but with falling temperature this compound

[1] Z. physikal. Chem., 1895, 17, 1.
[2] J. Amer. Chem. Soc., 1926, 48, 1207.

progressively dissolves hydrogen. Hanawalt[1] examined the effect of hydrogen on the X-ray absorption spectrum of palladium, and found a marked distension of the palladium lattice, due to adsorbed hydrogen ; he also obtained evidence for combination, possibly due to the formation of Pd_2H.

This class of hydrides which behave as solid solutions is much larger than was at one time supposed. The rare earth metals take up hydrogen in this way, though their hydrides were formerly supposed to belong to the class of saline hydrides, and to have such formulae as PrH_3, CeH_3, NdH_2. The careful investigations of Sieverts[2] and his students
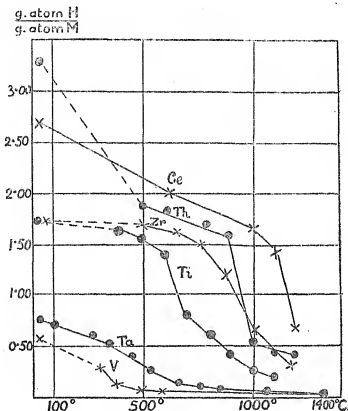
FIG. 80.—Some metal-hydrogen systems.

have shown that the black or metallic looking products obtained when these metals are heated in hydrogen are solid solutions. The relations between the quantity of hydrogen absorbed, the pressure and the temperature are similar to those which obtain for palladium. In general, besides palladium, those elements which occur from three to five places after a rare gas element in the long periods give hydrides of this sort—the rare earths, Ti, Zr, Th, V, Nb, Ta. The capacity for absorbing hydrogen increases in the same group with increasing atomic weight, e.g. from V to Ta, and diminishes in the same series with increase in atomic number, e.g. from La to Ta. The hydrogen content of some of these hydrides at various temperatures is given in Fig. 80,

[1] Proc. Nat. Acad. Sci., 1928, 14, 953.
[2] Z. anorg. Chem., 1923-26, 141-153 ; summary, Z. angew. Chem., 1929, 21, 37.

and it can be seen that the greater the quantity absorbed the higher the temperature at which the steep drop in the curve takes place.

The hydrogen is often taken up very readily; metallic lanthanum absorbs it even at room temperature. With commercial cerium the action begins above 300°, but if it is previously fused *in vacuo* the compact mass takes up great quantities of hydrogen at room temperature; formation of nitride inhibits the absorption completely. Different phases of these metal-hydrogen compounds can be distinguished by application of the methods of X-ray analysis. The arrangement of the atoms in the lattices obeys the same laws as in the nitrides, carbides and borides (*cf.* p. 852).

There are a number of "metal hydrides" which contain such large proportions of hydrogen that they may possibly be compounds, but which have been so little investigated that it is impossible to decide whether they are such or merely adsorption mixtures, solid solutions or "interstitial" compounds (see p. 302). The well-known copper hydride (p. 714) is an example. Again, when palladium salts are reduced in the presence of stabilising colloids (protalbinic acid, lysalbinic acid), a black palladium sol or gel is formed, which contains large quantities of hydrogen (Paal). Ethereal solutions of heavy metals in the presence of phenyl magnesium bromide give precipitates of hydrides when the gas is led through the solution.[1] The composition of these precipitates is as follows:

$$NiH_2 \quad CoH_2 \quad FeH_2 \text{ (from } FeCl_2) \quad FeH_6 \text{ (from } FeCl_3) \quad CrH_3 \quad WH >_3$$
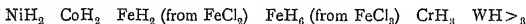
The lower arsenic hydride AsH, prepared by L. Moser and A. Bruckl, also probably belongs to this class. It is formed together with AsH_3 when Na_3As is hydrolysed and is a brown powder, easily oxidised in the air. When stannous salts are present another hydride is formed— the red As_4H_2, analogous to P_4H_2. The adsorption products of hydrogen and metals, such as FeH_2 (p. 872), which are active in ammonia synthesis, can also be included here. In all these cases adsorption and compound formation are somewhat similar processes which cannot be readily distinguished. Even the X-ray analysis gives no new evidence; in copper hydride, for instance, the atoms occupy the same positions as in metallic copper, except that they are further apart,[2] but the analogy with the behaviour of graphite and of carbides is significant.

Field Valency Hydrides.—These are probably the extreme members of the series of adsorption products. If iron or nickel is precipitated on the walls of a vessel very slowly in an atmosphere of hydrogen and on a support of some inert material such as NaCl, recrystallisation is largely prevented and each metal atom takes up six molecules of hydrogen. It can be shown that the NaCl takes up no hydrogen; and the action

[1] Weichselfelder, *Ann.*, 1926, 447, 64.
[2] Hüttig and Brodkorb, *Z. anorg. Chem.*, 1925, 153, 243.

is not mere occlusion, for inert gases are not taken up. Nitrogen, however, is absorbed but requires a greater proportion of inert support.[1] It may be supposed that the gas is attached to the metal atoms by field valencies and that these hydrides are analogous to metal ammines like $Ba(NH_3)_6$.

Saline Metallic Hydrides.—With the exception of magnesium, beryllium and the more strongly basic rare earths, all the alkali and alkaline earth metals form white crystalline compounds on heating with hydrogen. The formulae of these compounds can be derived from the ordinary valency of the metals, *e.g.* KH, CaH_2. These substances are true compounds and the hydrogen acts as a negative element, so that they deposit metal at the cathode and yield hydrogen at the anode when they are electrolysed in the molten condition, in accordance with the low position of hydrogen in the electromotive series.[2] This result is analogous to the electrolysis of the alloys mentioned on p. 864.

These hydrides can be formed in various ways, but while the alkaline earth metals combine with hydrogen with great rapidity on heating to a few hundred degrees, and even burn in the gas, the absorption of hydrogen by the alkali metals is exceptionally slow, and cannot generally be brought to completion at atmospheric pressure unless the hydride formed is sublimed off or the hydrogen is allowed to act on the vaporised or finely divided metal. With sufficiently high hydrogen pressure, the alkali hydrides can be obtained in greater quantity. The preparation of alkaline earth hydrides proceeds with greater facility at lower pressures. Lithium in this as in all other respects is analogous to the alkaline earth metals and not to the alkalis. Hydride formation takes place much more easily by the action of atomic hydrogen on the metal (see p. 116). All alkali metal hydrides have the crystal structure of rock-salt (p. 299).

The saline metallic hydrides are among the most reactive substances.[3] They are exceptionally susceptible to the action of water and twice the quantity of the hydrogen contained in them is evolved: $LiH + H_2O \longrightarrow LiOH + H_2$. This reaction, in conjunction with the oxidising action of atmospheric air, causes ignition when the hydride is damped in air. It is not surprising that they are strong reducing agents, so that, for example, CO_2 is reduced to carbon; they can absorb SO_2, which yields the hydrosulphite of the metal: $2NaH + 2SO_2 \longrightarrow Na_2S_2O_4 + H_2$. If the alkali hydrides are heated in an atmosphere of hydrogen they sublime with difficulty, giving colourless needles or aggregates like wadding. The hydrides conduct electricity only at high temperatures, when they are molten. The alkali hydrides cannot, however, be heated very much, since they

[1] Frankenburger, Meyrhofer and Schwamberger, *Z. Elektrochem.*, 1931, 37, 473.

[2] Moers, *Z. anorg. Chem.*, 1920, 113, 179.

[3] Moissan, *Compt. rend.*, 1902, 134, 71 ; 1903, 136, 591, 1522.

all decompose into the metal and hydrogen at 400°-500°. It is very remarkable that the dissociation temperatures of all these hydrides lie close together. The hydrides of the alkaline earths and of lithium behave quite differently on dissociation; on the one hand their dissociation temperatures are considerably higher than those of the alkali hydrides, that of lithium being the highest, then that of barium; and on the other hand they have no sharp dissociation point, but the temperature of decomposition rises with the quantity of hydrogen evolved, as the remaining hydride forms solid solutions with the metals set free.

It is probable that the formation of these salt-like hydrides precedes that of the alloys, so that the hydrogen may be both free and combined in the hydrides of other metals. The existence of the two forms of hydride may be noticed in those of the alkaline earths. When a little of the hydrogen is removed from calcium hydride a single phase of solid, poorer in hydrogen, is formed. Later in the decomposition this phase is resolved into a product containing more hydrogen and approaching CaH_2 in composition, and one containing less which retains it more firmly than CaH_2. On account of the formation of these mixtures the pressure-temperature equilibrium is only very slowly attained.

APPENDIX

THE LITERATURE OF INORGANIC CHEMISTRY

THE student should realise that the necessarily abbreviated statements in text-books such as this are based on original investigations, and for more complete information on any given subject it is necessary to refer to the original memoirs.

For instance, before commencing a research or undertaking the manufacture of a new product, it is essential to find out as completely as possible what work has already been carried out along the lines of the proposed investigation. The search is less simple in inorganic chemistry than in the organic branch, as the papers are more scattered and are not so simply indexed; otherwise the procedure is much the same. The first object should be to compile a complete list of references, and to this end all likely sources should be utilised. The larger treatises are first consulted, as they give at least the more important references; many of these works are in German and several are incomplete. The more useful are as follows (in alphabetical order):

> Friend: *Text-book of Inorganic Chemistry.*
> Gmelin-Kraut: *Handbuch der anorganischen Chemie.* (New edition, incomplete.)
> Hoffmann: *Lexikon der anorganischen Chemie.* (Incomplete; compounds indexed under empirical formulae.)
> Mellor: *Comprehensive Treatise on Inorganic Chemistry.*
> Moissan: *Traité de chimie minérale.*
> Pascal: *Traité de chimie minérale.*
> Thorpe and Whiteley: *Dictionary of Applied Chemistry.*
> Ullmann: *Enzyklopädie der technischen Chemie,* 2nd edition.

Older works than these should not be despised, as the abstracting of papers was far from complete up till a few years ago. The date of the volumes consulted should be noted, and it is convenient in the first instance to arrange the references in historical order.

These works will give more detailed accounts of the substance under investigation, and the less important and also the more recent papers will be sought in the various abstracts, the more important being:

British Chemical and Physiological Abstracts—A. Pure Chemistry and Physiology,
> *B. Applied Chemistry* (Bureau of Chemical and Physiological Abstracts, London).

> NOTE—Before 1924, corresponding abstracts are to be found in the *Journals of the Chemical Society and of the Society of Chemical Industry.*

Chemical Abstracts. (American Chemical Society.)
Chemisches Zentralblatt. (German Chemical Society.)

It may be pointed out that abstracts, however well done, are only a rough guide to the contents of the papers themselves. These must be considered

next, and all those which appear to be relevant to the matter in hand should be carefully read and the contents noted. Papers on inorganic chemistry appear in almost all chemical journals, many of which (together with the abstract journals quoted above) issue decennial or quinquennial indexes, the use of which makes it unnecessary to consult the indexes at the end of each volume. It should be noted that some of these journals form more than one volume per year, so it is always desirable to note both year and number of volume. The more important journals in which inorganic investigations are published are as follows:

Journal of the Chemical Society (London).
Journal of the American Chemical Society.
Journal of the Society of Chemical Industry.
Industrial and Engineering Chemistry.
Proceedings of the Royal Society.
Transactions of the Faraday Society.
Recueil des travaux chimiques des Pays-Bas.
Bulletin de la Société chimique de France.
          ,,   ,,   ,, *Belgique.*
Annales de Chimie (formerly *Annales de Chimie et de Physique*).
Comptes rendus (Académie des Sciences).
Helvetica Chimica Acta.
Annalen der Chemie.
Berichte der deutschen chemischen Gesellschaft.
Journal für praktische Chemie.
Monatshefte für Chemie.
Zeitschrift für anorganische und allgemeine Chemie.
    ,,   ,, *angewandte Chemie.*
    ,,   ,, *Elektrochemie.*
    ,,   ,, *physikalische Chemie.*
Gazetta chimica italiana.

There are, of course, a very large number of other journals, some of which confine their attention to particular branches of the subject. Those in the above list should be available in any good chemical library; a very complete set of both books and journals is to be found in the library of The Chemical Society in London.

By proceeding in this way it is possible to obtain reasonably complete information about a given substance, but it is less easy to find out what is known about a general phenomenon, *e.g.* the electrolysis of fused salts, though there is often a monograph or report on subjects which have been at all well investigated. The reports of the Committees and Research Associations connected with the Department of Scientific and Industrial Research (published by H.M. Stationery Office), as well as those of the Bureaux of Standards, Mines, etc., and other Government departments of the U.S.A., often contain matter not published elsewhere. The Annual Reports on the Progress of Chemistry (published by the Chemical Society) and those on the progress of Applied Chemistry (published by the Society of Chemical Industry) give valuable summaries of the important work done each year. The subdivision of chemistry into "pure" and "applied" should not be taken too seriously, and when the papers are separately indexed under these two headings both indexes should be consulted, unless the matter under investigation is extremely theoretical.

ATOMIC WEIGHTS AND ATOMIC NUMBERS (1941)

Atomic No.		Symbol.	Atomic Weight.	Atomic No.		Symbol.	Atomic Weight.
13	Aluminium	Al	26·97	60	Neodymium	Nd	144·27
51	Antimony	Sb	121·76	10	Neon	Ne	20·183
18	Argon	A	39·944	28	Nickel	Ni	58·69
33	Arsenic	As	74·91	41	Niobium Nb (=Columbium Cb)		92·91
56	Barium	Ba	137·36	7	Nitrogen	N	14·008
4	Beryllium Be (=Glucinum Gl)		9·02	76	Osmium	Os	190·2
83	Bismuth	Bi	209·00	8	Oxygen	O	16·0000
5	Boron	B	10·82	46	Palladium	Pd	106·7
35	Bromine	Br	79·916	15	Phosphorus	P	30·98
48	Cadmium	Cd	112·41	78	Platinum	Pt	195·23
55	Caesium	Cs	132·91	19	Potassium	K	39·096
20	Calcium	Ca	40·08	59	Praseodymium	Pr	140·92
6	Carbon	C	12·010	91	Protoactinium	Pa	231
58	Cerium	Ce	140·13	88	Radium	Ra	226·05
17	Chlorine	Cl	35·457	86	Radon	Rn	222
24	Chromium	Cr	52·01	75	Rhenium	Re	186·31
27	Cobalt	Co	58·94	45	Rhodium	Rh	102·91
29	Copper	Cu	63·57	37	Rubidium	Rb	85·48
66	Dysprosium	Dy	162·46	44	Ruthenium	Ru	101·7
68	Erbium	Er	167·2	62	Samarium	Sa	150·43
63	Europium	Eu	152·0	21	Scandium	Sc	45·10
9	Fluorine	F	19·00	34	Selenium	Se	78·96
64	Gadolinium	Gd	156·9	14	Silicon	Si	28·06
31	Gallium	Ga	69·72	47	Silver	Ag	107·880
32	Germanium	Ge	72·60	11	Sodium	Na	22·997
79	Gold	Au	197·2	38	Strontium	Sr	87·63
72	Hafnium	Hf	178·6	16	Sulphur	S	32·06
2	Helium	He	4·003	73	Tantalum	Ta	180·88
67	Holmium	Ho	164·94	52	Tellurium	Te	127·61
1	Hydrogen	H	1·0080	65	Terbium	Tb	159·2
49	Indium	In	114·76	81	Thallium	Tl	204·39
53	Iodine	I	126·92	90	Thorium	Th	232·12
77	Iridium	Ir	193·1	69	Thulium	Tm	169·4
26	Iron	Fe	55·85	50	Tin	Sn	118·70
36	Krypton	Kr	83·7	22	Titanium	Ti	47·90
57	Lanthanum	La	138·92	74	Tungsten	W	183·92
82	Lead	Pb	207·21	92	Uranium	U	238·07
3	Lithium	Li	6·940	23	Vanadium	V	50·95
71	Lutecium	Lu	174·99	54	Xenon	Xe	131·3
12	Magnesium	Mg	24·32	70	Ytterbium	Yb	173·04
25	Manganese	Mn	54·93	39	Yttrium	Y	88·92
80	Mercury	Hg	200·61	30	Zinc	Zn	65·38
42	Molybdenum	Mo	95·95	40	Zirconium	Zr	91·22

THE PERIODIC CLASSIFICATION

(The figures in heavy type are the atomic numbers, the others the atomic weights)

0.	I. a	I. b	II. a	II. b	III. a	III. b	IV. a	IV. b	V. a	V. b	VI. a	VI. b	VII. a	VII. b	VIII.
1 H 1·0080															
2 He 4·003	3 Li 6·940		4 Be 9·02		5 B 10·82		6 C 12·010		7 N 14·008		8 O 16·0000		9 F 19·00		
10 Ne 20·183	11 Na 22·997		12 Mg 24·32		13 Al 26·97		14 Si 28·06		15 P 30·98		16 S 32·06		17 Cl 35·457		
18 A 39·944	19 K 39·096		20 Ca 40·08		21 Sc 45·1		22 Ti 47·90		23 V 50·95		24 Cr 52·01		25 Mn 54·93		26 Fe 55·85 27 Co 58·94 28 Ni 58·69
36 Kr 83·7		29 Cu 63·57		30 Zn 65·38		31 Ga 69·72		32 Ge 72·60		33 As 74·91		34 Se 78·96		35 Br 79·916	
	37 Rb 85·48		38 Sr 87·63		39 Y 88·92		40 Zr 91·22		41 Nb 92·91		42 Mo 95·95		43 Ma		44 Ru 101·7 45 Rh 102·91 46 Pd 106·7
54 Xe 131·3		47 Ag 107·880		48 Cd 112·41		49 In 114·76		50 Sn 118·70		51 Sb 121·76		52 Te 127·61		53 I 126·92	
	55 Cs 132·91		56 Ba 137·36		57 La 138·92	58-71 Ce, etc.*	72 Hf 178·6		73 Ta 180·88		74 W 183·92		75 Re 186·31		76 Os 190·2 77 Ir 193·1 78 Pt 195·23
86 Rn 222		79 Au 197·2		80 Hg 200·6		81 Tl 204·39		82 Pb 207·21		83 Bi 209·00		84 Po 210·0		85—	
	87—		88 Ra 226·05		89 Ac 227		90 Th 232·12		91 Pa 231		92 U 238·07				

* Rare earths : 58 Ce 140·13, 59 Pr 140·92, 60 Nd 144·27, 61 Il, 62 Sa 150·43, 63 Eu 152·0, 64 Gd 156·9, 65 Tb 159·2, 66 Dy 162·46, 67 Ho 164·94, 68 Er 167·2, 69 Tm 169·4, 70 Yb 173·04, 71 Lu 174·99

CRYSTAL STRUCTURE

I. **Elements** (for diagrams and examples see pp. 19-21).

  (a) Face-centred cubic lattice.

  (b) Body-centred cubic lattice.

  (c) Hexagonal close packing.

  (d) Diamond lattice.

  (e) Graphite lattice.

II. **Compounds AX.**

  (a) *Face-centred lattice* (Fig. 46, p. 299).

    Halides of alkali metals (CsCl, CsBr, CsI at higher temperatures)
      AgF, AgCl, AgBr.

    MgO, CaO, SrO, BaO, CdO, FeO, CoO, NiO.

    MgS, MgSe, CaS, CaSe, CaTe, SrS, SrSe, SrTe, BaS, BaSe,
      BaTe, MnS, MnSe, PbS, PbSe, PbTe, SnTe.

    TiN, ZrN, VN, NbN; NbC; LiH, NaH.

  (b) *CsCl lattice* (Fig. 33, p. 239).

    CsCl, CsBr, CsI, NH₄Cl, NH₄Br, NH₄I, TlCl, TlBr, TlI.

    TlBi, CuZn, AgZn, AuZn, AlNi.

  (c) *Zinc blende lattice.*
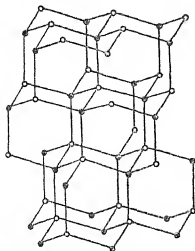
CuCl, CuBr, CuI.
ZnS, ZnSe, ZnTe, HgS, HgSe, HgTe,
  BeS, BeTe, CdS, CdSe, CdTe.
AlP, AlAs, AlSb, InSb, SaP, GaAs,
  GaSb, SnSb.
CSi.

FIG. 81.

(d) *Wurtzite lattice.*
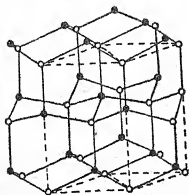
ZnS, CdS, CdSe.
BeO, ZnO.
AlN, NH$_4$F.

Fig. 82.

(e) *Boron nitride lattice.*   BN.
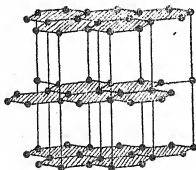
Fig. 83.

(f) *Nickel arsenide lattice.*
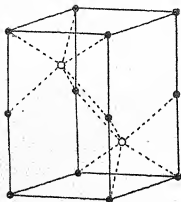
FeS, FeSe, CoS, CoSe, CoTe, NiS, NiSe
     NiTe.
NiAs, NiSb, MnSb, TeSb, CoSb.

Fig. 84.

III. Compounds AX_2.

(a) *Fluorite lattice* (Fig. 36, p. 258).

CaF_2, SrF_2, BaF_2, $SrCl_2$, CdF_2, PbF_2.

CeO_2, PrO_2, ZrO_2, ThO_2, UO_2, Li_2O, Na_2O.

Li_2S, Na_2S, Cu_2S, Cu_2Se.

Mg_2Si, Mg_2Sn, Mg_2Pb.

(b) $[Co(NH_3)_6]I_2$ *lattice*.
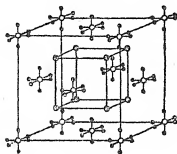
$[Co(NH_3)_6]I_2$; $K_2[PbCl_6]$; $(NH_4)_2[SiF_6]$.

FIG. 85.

(c) *Pyrites lattice*.
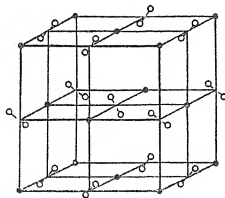
MnS_2, FeS_2, CoS_2, NiS_2, RuS_2, OsS_2, PtS_2.

FIG. 86.

(d) *Cuprite lattice*.
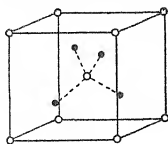
Cu_2O, Ag_2O.

FIG. 87.

(e) *Rutile lattice.*
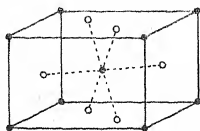
FIG. 88.

MnF_2, ZnF_2, FeF_2, CoF_2, NiF_2.
TiO_2, GeO_2, SnO_2, PbO_2, VO_2, NbO_2,
TeO_2, MoO_2, WO_2, MnO_2, RuO_2,
OsO_2, IrO_2.

(f) *Cadmium iodide lattice.*
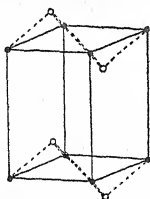
FIG. 89.

CdI_2, SbI_2.
$Mg(OH)_2$, $Ca(OH)_2$, $Cd(OH)_2$.
TiS_2, $TiSe_2$, ZrS_2, $ZrSe_2$, SnS_2.

(g) *Molybdenite lattice.*
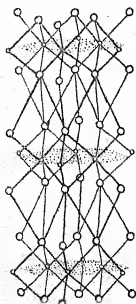
FIG. 90.

MoS_2, WS_2.

(h) *β-Cristobalite.* SiO_2.
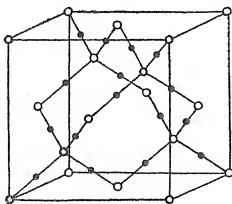
FIG. 91.

(i) *Calcium carbide lattice.*
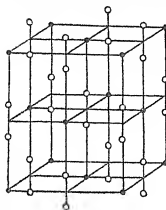
FIG. 92.

CaC_2, SrC_2, BaC_2, LaC_2, CeC_2, PrC_2, NdC_2.

IV. Compounds AX_3 and AX_4.

(a) *Sodium hydrofluoride lattice.*

FIG. 93.

$NaHF_2$, NaN_3, $CaCN_2$.

(b) *Calcite lattice.*

$CaCO_3$, $MgCO_3$, $ZnCO_3$, $MnCO$
$FeCO_3$.
$NaNO_3$.
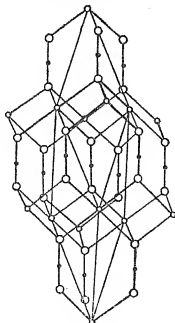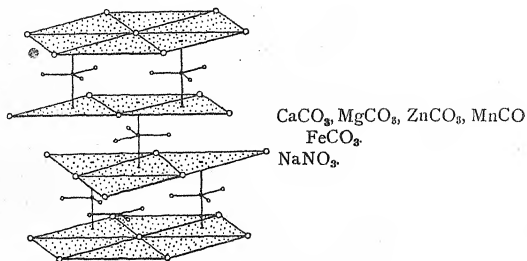
Fig. 94.

(c) *Aragonite lattice.*

$CaCO_3$, $SrCO_3$, $BaCO_3$.
KNO_3; $LaBO_3$.
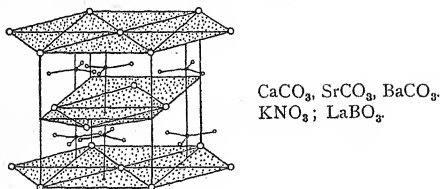
Fig. 95.

V. **Silicates** (see pp. 826-828).

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A TEXT-BOOK OF

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